

## Supporting information

### Base-free, switchable, Au-catalyzed oxidative esterification of alcohols in continuous flow

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#### 1. Determining the flow regime of the reactors

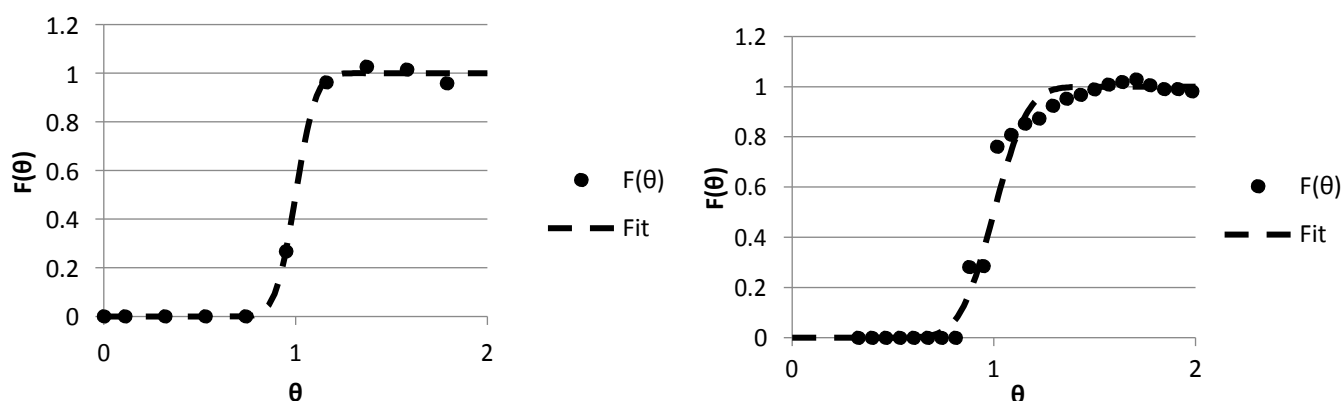
The Peclet numbers (Pe) for each of the reactors were determined by tracer experiments.

The resulting breakthrough curve,  $F(t)$  is the integral over time of the  $E$  curve:

$$F(t) = \int_0^t E(t) dt$$

To determine the Peclet number, equation (3) was entered into Berkeley Madonna (<http://www.berkeleymadonna.com>), a differential equation solver, as the differential equation of  $F(\theta)$ , and the breakthrough curves were fitted to this to obtain  $D/UL$ .

The breakthrough curve (Fig S1) for the reactor was measured *without a packed bed* at a total flow rate of 0.5 mL min<sup>-1</sup>. A solution of benzyl alcohol in *tert*-butanol (0.25 M) was used as the tracer. The eluent was collected as 0.5 mL aliquots, from which 100  $\mu$ L was extracted and diluted with 0.8 mL of solvent (1:1 v/v *tert*-butanol:2-methyl-2-butanol) containing an external standard (4-chlorobenzyl alcohol, 17 mM) for GC analysis.



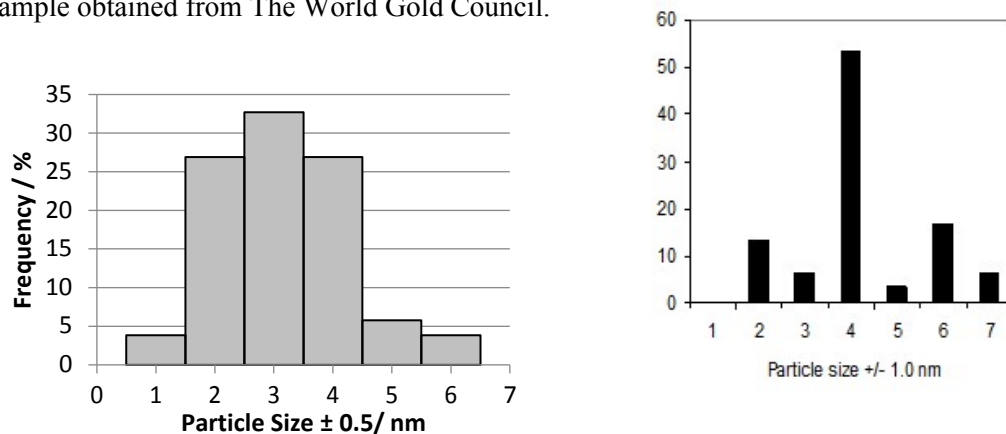
**Fig. S1:** Breakthrough curves for X-Cube (left) and for the custom reactor (right), including fit to a plug flow reactor model

The breakthrough curves were plotted as the tracer concentration in the eluent,  $C$ , normalised by the feed tracer concentration,  $C_0$  against  $\theta$ , assuming a constant flow rate,  $C/C_0 = E(\theta)$ . The data was fitted to the model in Berkeley Madonna by floating  $D/UL$ , affording Peclet numbers,  $Pe = 286$  (X-Cube) and  $Pe = 116$  (custom reactor), confirming operation of plug flow in both systems.

#### 2. Catalyst characterisation

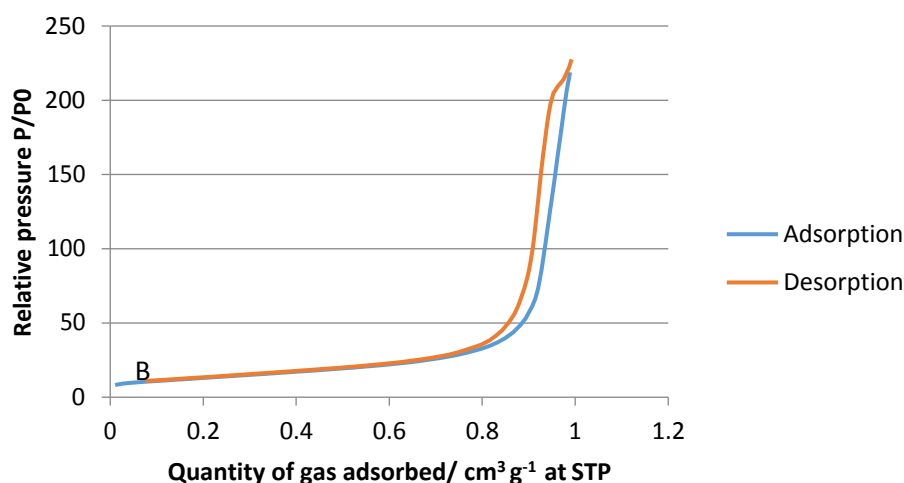
For the experiments performed with benzyl alcohol, 1% Au/TiO<sub>2</sub> catalyst was commercially procured from Strem (AUROLite™ Au/TiO<sub>2</sub>) as extrudites, which were ground and sieved to 45-53  $\mu$ m. The same sample was used for all

the kinetic studies. TEM analysis was carried out using a JEOL JEM2100 F/HT microscope (line resolution=0.14 nm) fitted with an EM-21010-21020 single tilt sample holder and an Orius 1000 camera. An Energy Dispersive X-Ray Spectrometer (EDS) from Oxford Instruments was used to determine which elements were present in the images, although the scope was too broad to measure individual nanoparticles of less than 10 nm. Samples were prepared by suspending fine particles of the catalyst in methanol. A drop of this suspension was then placed on a carbon grid support, allowed to dry, then loaded into the machine. At magnifications between 80k and 400k, photographs were taken, from which the sizes of the metal nanoparticles were measured. It should be noted that limits to the resolution of the images mean that nanoparticles smaller than 1 nm were difficult to measure. The histograms for the Strem Au/TiO<sub>2</sub> showed that 50% of the nanoparticles measured in the size range 3-4 nm (Fig. S2), which is similar to the sample obtained from The World Gold Council.



**Fig. S2:** Particle size distributions of catalysts **S1** (left, 52 counts) and **S2** (right, 100 counts)

**BET (Brunauer–Emmett–Teller) analysis:** 0.15 g sample of catalyst was degassed by heating the sample at 100 °C under nitrogen for 12 hours. BET measurement was carried out with N<sub>2</sub> gas at 77 K on Tristar 3000 (Micromeritics Instrument Corporation, version 6.07). The results are shown in the Table S1.

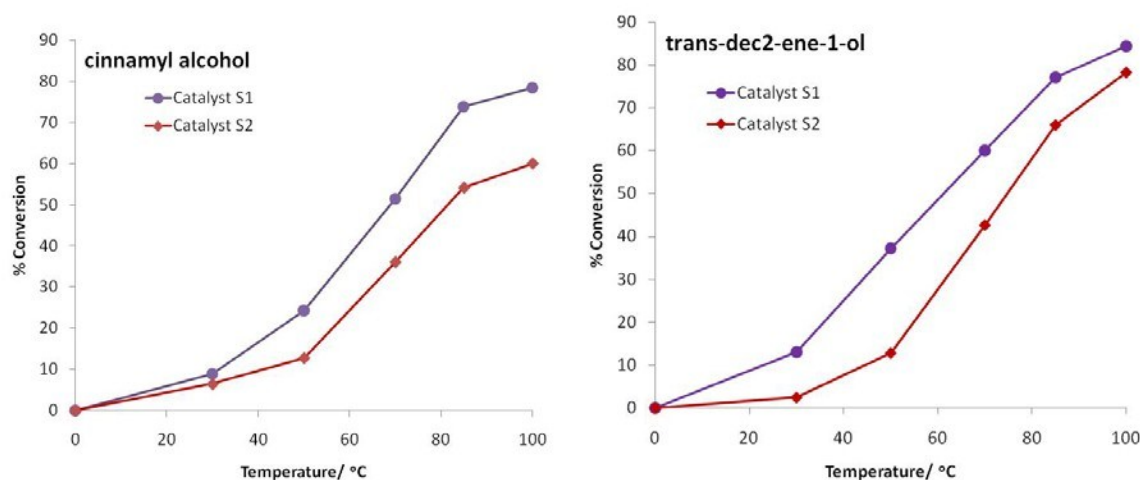


**Fig. S3:** N<sub>2</sub> adsorption and desorption isotherms for catalyst **S1** at 77K

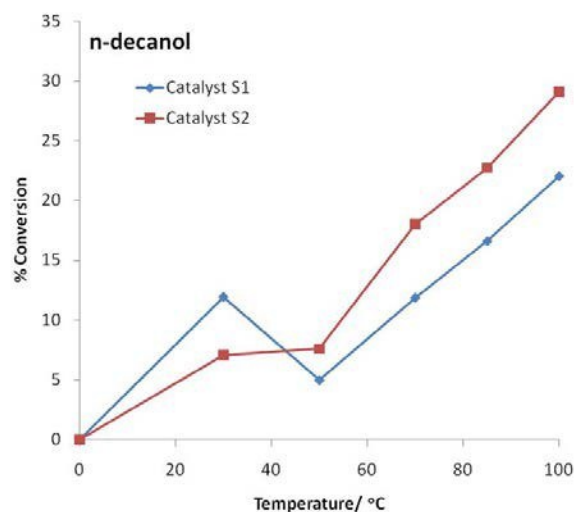
**Table S1.** Surface area and micropore volume for catalysts, determined by BET.

Catalyst	particle size = 90-106 $\mu\text{m}$	particle size = 45-53 $\mu\text{m}$
Surface area / $\text{m}^2 \text{g}^{-1}$	$46.6 \pm 0.2$	$47.5 \pm 0.2$
Pore Volume	0.32	0.30

The same batch of catalyst was ground and sieved into different support size ranges; therefore, two different mesh size ranges were tested to ensure that the surface area had not been greatly affected.

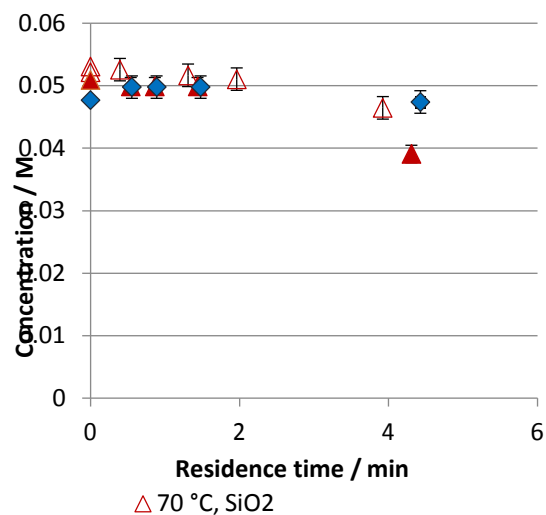


**Fig. S4:** Single-pass conversions for the Au-catalysed oxidation of cinnamyl alcohol (left) and decenol (right). Conditions: 10-fold excess of  $\text{H}_2\text{O}_2$  at different temperatures, using S1 and S2. Selectivity is  $>98\%$  for the aldehyde in both cases.

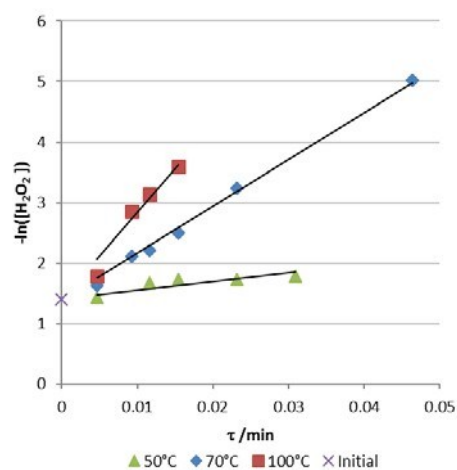


**Fig. S5:** Single-pass conversions for the Au-catalysed oxidation of n-decanol in the presence of 10-fold excess of  $\text{H}_2\text{O}_2$  at different temperatures, using S1 and S2. *The first data point obtained with S1 is an outlier, which is due to the large error associated with the low level of conversion.*

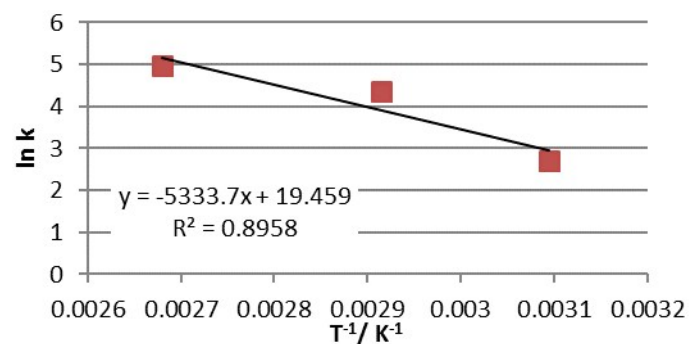
## Decomposition of H<sub>2</sub>O<sub>2</sub>



**Fig. S6:** Decomposition of 50 mM H<sub>2</sub>O<sub>2</sub> in MeOH/H<sub>2</sub>O (1:1 v/v) over a silica or silica/titania packed bed, flow rate = 0.2 – 1.6 mL/min.

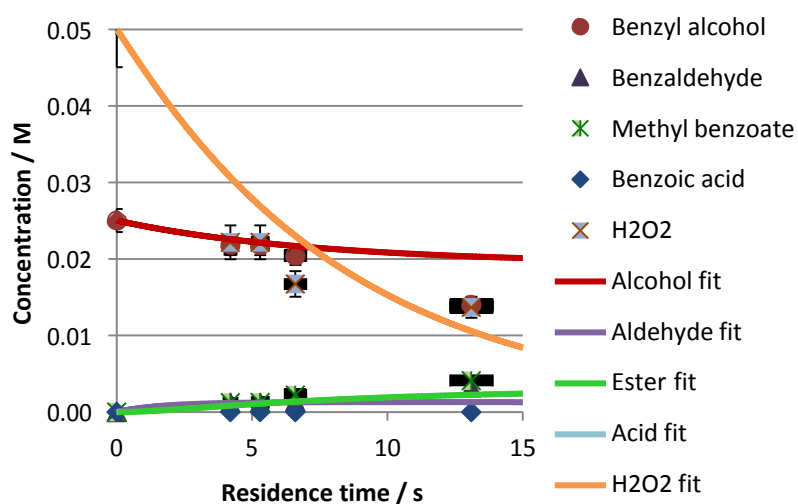


**Fig. S7.** Decomposition of H<sub>2</sub>O<sub>2</sub> over Au/TiO<sub>2</sub> at different temperatures.

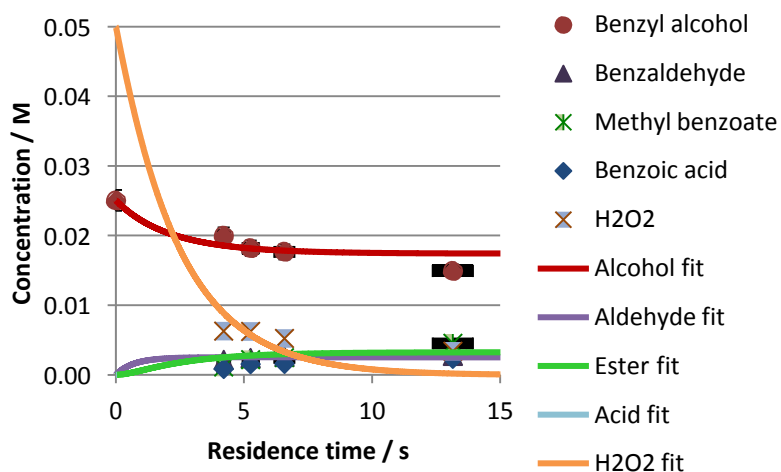


**Fig. S8:** Arrhenius plot for H<sub>2</sub>O<sub>2</sub> decomposition over Au/TiO<sub>2</sub>.

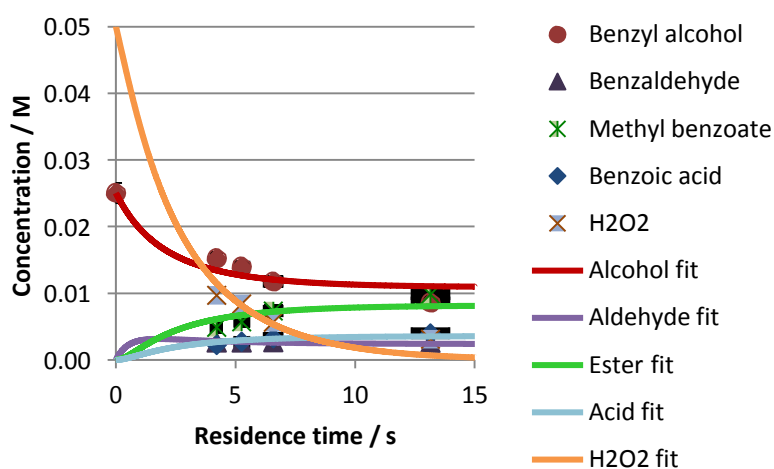
**Kinetic data fitting using benzyl alcohol as precursor:** Reaction conditions: 25 mM benzyl alcohol, 50 mM H<sub>2</sub>O<sub>2</sub>, 200 mg Au/TiO<sub>2</sub>, MeOH/H<sub>2</sub>O (1:1 v/v), 200 psi, flow rates =0.8-2.5 mL/min.



**Figure S9.** Reaction recorded at 50 °C. RMS = 0.0073.

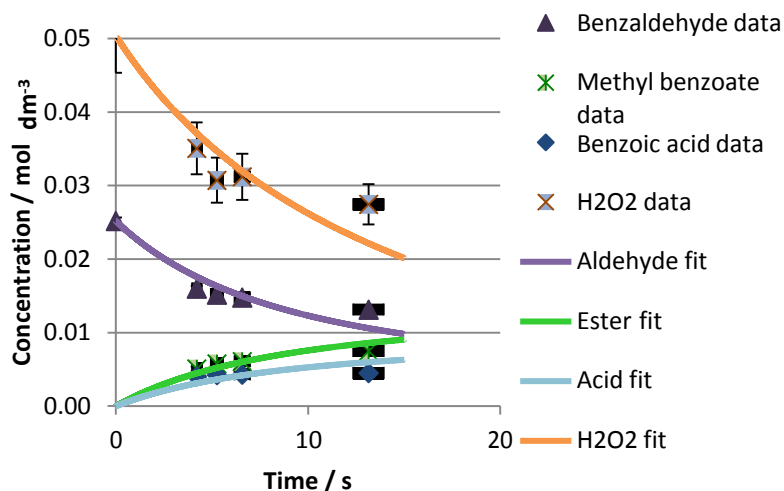


**Figure S10.** Reaction recorded at 70 °C. RMS = 0.0049.

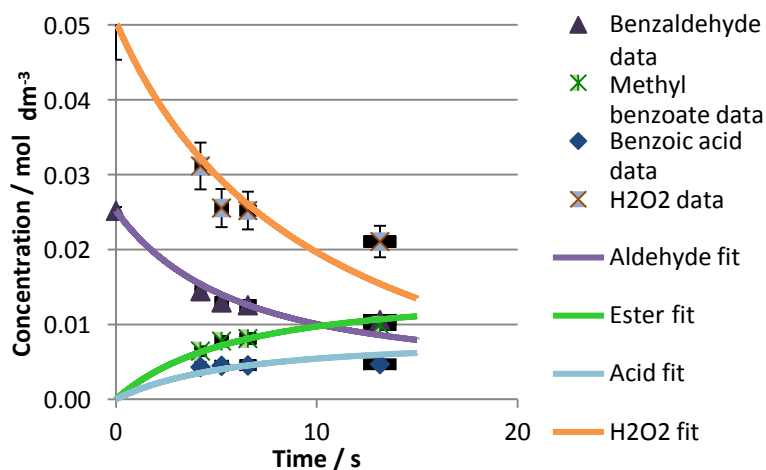


**Figure S11.** Reaction recorded at 100 °C. RMS = 0.0044.

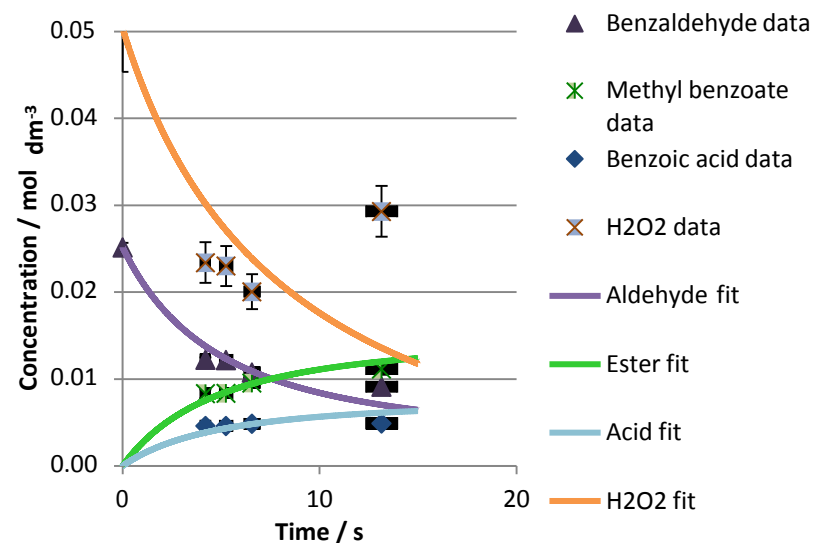
**Kinetic data fitting using benzaldehyde as precursor:** Reaction conditions: 25 mM benzaldehyde, 50 mM H<sub>2</sub>O<sub>2</sub>, 200 mg Au/TiO<sub>2</sub>, MeOH/H<sub>2</sub>O (1:1 v/v), 200 psi, flow rates = 0.8-2.5 cm<sup>3</sup> min<sup>-1</sup>



**Figure S12:** Reaction recorded at 35 °C. RMS = 0.0059.



**Figure S13:** Reaction recorded at 50 °C. RMS = 0.0052.



70 °C

Model fit root mean squared error = 0.01

H<sub>2</sub>O<sub>2</sub> fit appears to be distorted by the data point at 13 s

**Figure S14:** Reaction recorded at 70 °C. RMS = 0.01 (H<sub>2</sub>O<sub>2</sub> fit is distorted by outlying data point at 13 s).

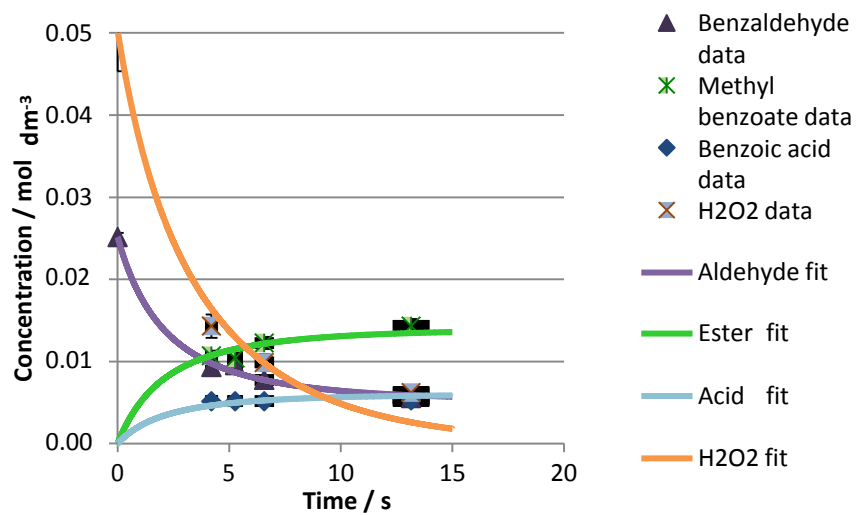


Figure S15: Reaction recorded at 100 °C. RMS = 0.0035

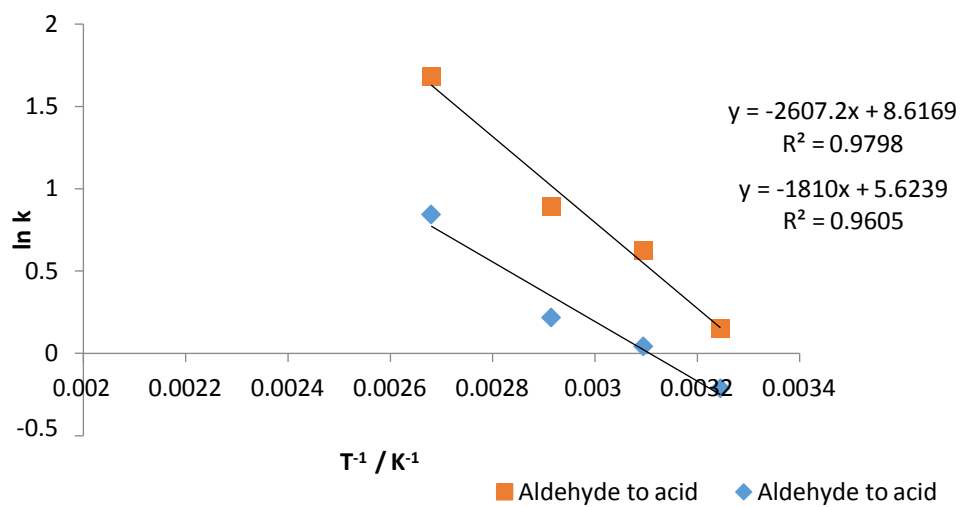


Fig. S16: Arrhenius plot for benzaldehyde oxidation.