Supplementary Information

Catalytic conversion of glycerol to allyl alcohol; effect of a sacrificial reductant on the product yield

Gizelle Sanchez[a], Jarrod Friggieri[a], Adesoji A. Adesina[b], Bogdan Dlugogorski[c], Eric M. Kennedy[a] and Michael Stockenhuber[a*]

[a] Priority Research Centre for Energy (PRCfE). The University of Newcastle, Callaghan, NSW 2308, Australia.
[b] ATODATECH LLC, Brentwood, CA 94513, USA.
[c] School of Engineering and Information Technology. Murdoch University, Murdoch, WA 6150, Australia.

Economic evaluation

A brief economic evaluation was carried out, with the assumption that a potential scale up of the catalytic reactions would result in the same yield of allyl alcohol as that obtained in the experimental studies. This enabled a rough estimation of the feasibility of the studied processes. Calculations were performed on the basis of 10 tonne of allyl alcohol produced over the iron catalyst in the absence of additives. The allyl alcohol market price employed in the assessment was equal to 2200/tonne as reported in ([1],[2]).

Table 1. Economic evaluation of the use of sacrificial reductants in the production of allyl alcohol over an alumina supported iron catalyst

	Ammonia	Ammonium hydroxide	Oxalic acid	Formic acid
Allyl alcohol yield (%)	11.3	15.1	17.8	19.5
Quantity of additive required (%)	3 v/v	10 wt	7 wt	33 wt
Additional production of allyl alcohol (tonne)	3.3	7.8	10.9	12.9
Revenue (USD)	7200	17000	24000	28000
Quantity of additive required (tonne)	1.3	52.7	38.7	187.1
Price of additive per tonne (USD)	390 [3]	260 [1]	560 [4]	600 [3]
Cost (USD)	500	14000	22000	110000
Net profit for excess production (USD)	6700	3000	2000	-82000
Increase in profit with the use of additives with respect to application of no additives (%)	**30.6**	**15.3**	**11.2**	
Benefit/Cost	14.1	1.2	1.1	0.3

The use of ammonia and ammonium hydroxide as sacrificial reductants increased the net profitability by approximately 30 % and 15 %, respectively, when compared to the

manufacture of allyl alcohol in the absence of additives (table 1). For ammonia, this is due to the relatively low quantity of additive required (1.3 tonne), to enhance the rate of formation of allyl alcohol (in excess of 3.3 tonnes). Oxalic acid has a higher market value than ammonia and ammonium hydroxide, which explains the lower increase in the net benefit (10 %). Even though the highest yield of allyl alcohol was obtained for co-feeding formic acid, this process was not economically feasible for the production of allyl alcohol due to the high concentration of the additive required. As mentioned in the manuscript, when comparing with experiments conducted in the presence of oxalic acid, differences between the amount of the additive required to produce a similar effect on the yield of allyl alcohol were not stoichiometric. The cost of co-feeding formic acid with glycerol exceeds any benefit obtained from doubling the yield of allyl alcohol. However at laboratory scale, the importance of the catalysed and continuous processes relies on the understanding of the mechanism taking place to enhance the yield of the desired product. The similarity of the formic acid with the oxalic acid molecule prompted us to explore the use of formic acid in the investigation of reaction pathways.
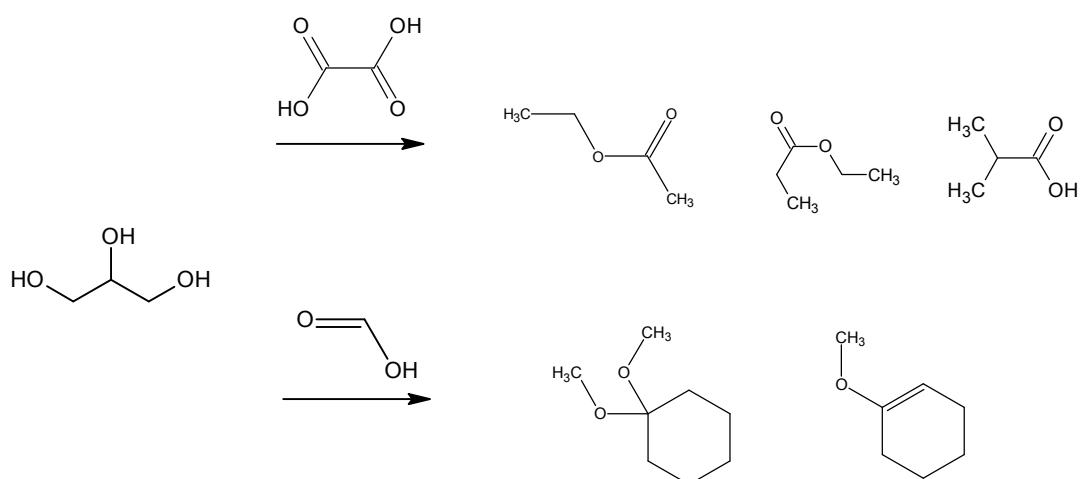

Figure S1. Scheme for conversion of glycerol in the presence of sacrificial reductants, exclusive products to the use of oxalic and formic acids.

References

1.   ICIS, *ICIS Chemical Business Americas*.
2.   D. T. Johnson and K. A. Taconi, *Environmental Progress*, 2007, **26**, 338-348.
3.   I. C. Business, *Chemical Market Reporter*.
4.   *China Chemical Reporter*.