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The use of alkaline earth oxides as pH modifiers for selective glycerol oxidation over supported Au catalysts.

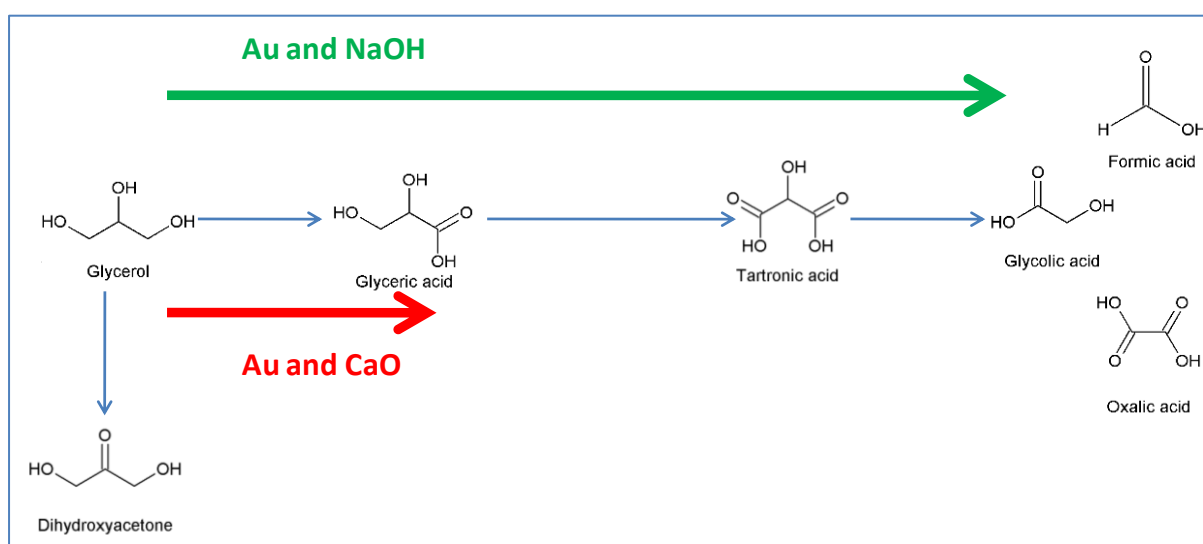
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Highlights.

- CaO and BaO can modify reaction pH and allow glycerol selective oxidation
- Ca²⁺ and Ba²⁺ stabilize glyceric acid against oxidation – affecting selective oxidation selectivity
- Au nanoparticles on CaO are active selective oxidation catalysts without other base modifiers

Graphical Abstract



Abstract.

The activity and selectivity of an Au/TiO₂ catalyst in a reaction mixture which has had its pH adjusted by the addition of NaOH (aq) is compared to that of the same catalyst in reaction mixtures whose pH was adjusted using suspensions of BaO and CaO.

It was found that the suspensions acted as effective bases and reactions in their presence showed similar conversions to those where NaOH(aq) was used. The selectivities of the reactions were different in each case. In all cases dihydroxyacetone, glyceric acid, glycolic acid and formic acid was produced but more glyceric acid was produced when alkaline earth oxide suspensions were used (at the expense of glycolic and formic acid) than when NaOH(aq) was used.

Given glycolic and formic acids are produced from oxidation of glyceric acid, it seems that glyceric acid is somewhat stabilized against further oxidation in the presence of the group II oxides. One explanation for this is the formation of glyceric acid hemicalcium salts (and analogous Ba²⁺ species) in solution.

Keywords: glycerol oxidation, basic materials, group II oxides.

1. Introduction

One of the side effects of the use of bio-derived triglycerides as feedstocks for the production of Fatty Acid Methyl Esters (FAME) biodiesel is the generation of large volumes of glycerol. This is a side-product of the transesterification of triglycerides into FAME through reaction with methanol [1-4]. The use of this material to generate value-added products would improve the economics FAME production and, to this end, there have been significant advances in glycerol valorisation through oxidation [5-8], reforming [9] and etherification [10-11] reactions.

Regarding glycerol oxidation using O_2 , a range of products can be produced. Oxidation at the 1° OH groups leads to the formation of glyceric acid which can undergo further oxidation (forming tartronic acid) and C-C bond cleavage reactions to form glycolic, oxalic and formic acids. Oxidation at the 2° OH group leads to the formation of dihydroxyacetone. Further oxidation of this material may lead to the formation of hydroxypyruvic and mesoxalic acids.

These products have several roles in the wider chemical industry, e.g. dihydroxyacetone, can be used in the cosmetics industry [12], glyceric acid can be used in the production of detergents and skin creams [13] and tartronic acid can be used as a chelating agent and in the synthesis of fine chemicals and novel polymers [14]. Furthermore, C-C bond cleavage during oxidation can lead to the selective production of glycolic and oxalic acids as well as formic acid (see figure 1).

It has generally been found that the selective oxidation reaction proceeds over supported Pd or Au nanoparticles [15-20] and under basic conditions. There have also been reports of base free oxidations [21-24].

Figure 1

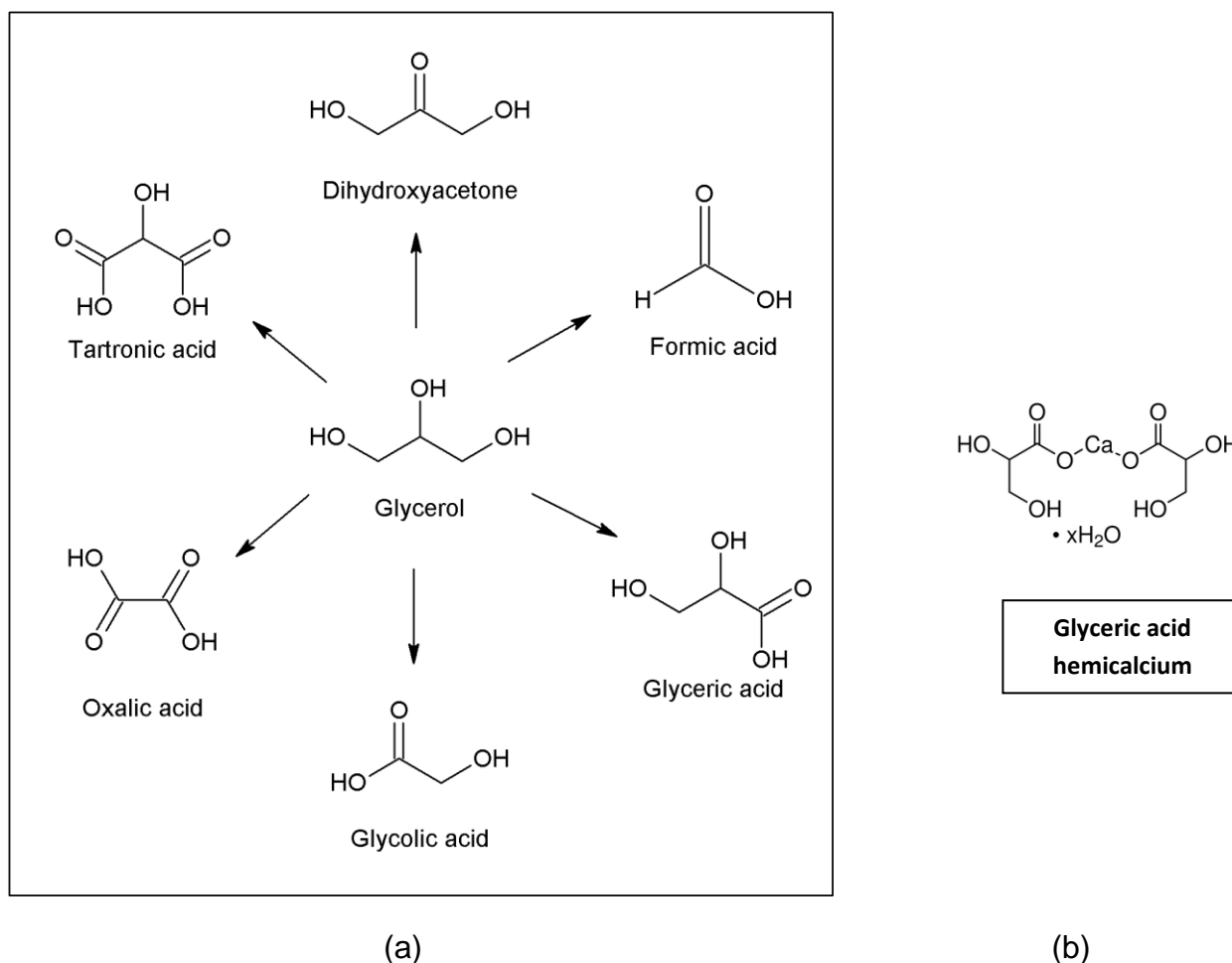


Figure 1. Possible products following selective oxidation of Glycerol using O_2 (a). The structure of glyceric acid hemicalcium is also shown (b)

Normally, aqueous NaOH serves as the base in this reaction although Hutchings *et al.* [25] have shown that the nature of the aqueous base is important in directing product selectivity over a Pt/C catalyst. These workers have also shown that the use of MgO as a support for Au-Pt catalysts generates active catalysts for the selective oxidation reaction under base-free conditions (when the reaction is carried under a 3 atm. O_2) [26]. Claus *et al.* have used combinations of aqueous and solid phase bases in promotion of the reaction (also under 10 atm. O_2) and have found that

Au/MgO was less active than an Au/C analogue [27]. The current work looks at activity under atmospheric pressure.

Solid bases such as group II oxides and carbonates have received recent attention as basic catalysts and supports [28, 29] but, to our knowledge; have never been used as pH modifying agents in these selective oxidation reactions. In this work we have compared the activity and selectivity of a standard Au/TiO₂ catalyst in the selective oxidation reaction when NaOH(aq), CaO(s) and BaO(s) are used as basic agents within the reaction under ambient pressure. We have also looked at the activity and selectivity of Au/CaO and Au/BaO catalysts in the promotion and selectivity of the reaction and the effect of dissolved Ca²⁺ species on selectivity.

2.0 Experimental

2.1 Catalyst Preparation

TiO₂ (from Degussa) was pre-densified before use by wetting with deionised water followed by calcination at 550 °C for 2 h. Following calcination the material was ground finely using a pestle and mortar. The 1% Au/TiO₂ catalyst was prepared using a standard deposition precipitation procedure [30].

An aqueous solution of H₂AuCl₄·3H₂O (ACS reagent, ≥ 49.0 % Au basis – Sigma-Aldrich) (0.02 g, 5.08 × 10⁻⁵ mol, 20 mL, clear yellow solution) was added to an aqueous solution of urea (99 +% ACS reagent) (0.61 g, 1.02 × 10⁻² mol, 20 mL,

colourless solution) and heated to 80 °C with stirring resulting in the formation of a clear yellow solution. Sodium citrate (5.08×10^{-5} mol) and TiO₂ (1 g) was added and the slurry was stirred for 4 h. The solid was then filtered, washed thoroughly with deionised water (ensuring that the filtrate was free of chloride using a standard AgNO₃ test), dried at 80 °C for 2 h and stored in a refrigerator until required. Prior to its use in a reaction, the dried material was activated by calcination in static air at 300 °C for 4 h.

2.2 Au/TiO₂ Characterisation

The Au/TiO₂ catalyst was characterised using a range of techniques including Elemental Analysis involved AA (Spectra AA 55B Atomic Absorption spectrometer), XPS analysis (Kratos AXIS Ultra DLD), UV Vis spectroscopy (Analytik Jena equipped with a SPECORD integrating sphere), TEM (Tecnai G2 20 Twin TEM-FEI) showed Au particles of ~ 5 nm (+/- 1.7 nm n = 200) and BET analysis (NOVA 2200e Surface Area and Pore Analyser, Quantachrome Instruments).

2.3 Catalytic reactions.

Catalytic reactions were carried out in a 250 mL three-necked flask, equipped with a septum, a Liebig condenser and a sparge on each of the necks. Experiments were carried out over 4 hours under atmospheric pressure using a flow of air, delivered into the solution through the sparge. The solution was stirred at a rate of 600 rpm.

Aqueous glycerol (0.5 M, 100 mL) was used as the substrate and reactions were carried out at 60 °C.

Aliquots of the mixture were removed using a 1 mL syringe equipped with a long needle through the septum, filtered through a 0.2 µm membrane and then diluted (100 µL reaction solution with 900 µL 0.01 N H₂SO₄). Post-reaction, the reaction solution was filtered using Whatman Grade 1 Qualitative filter paper circles in order to retrieve the catalyst.

Products from selective oxidation reactions were analysed using HPLC. The instrument was an Agilent Technologies 1200 series HPLC equipped with a degasser (G1322A), quaternary pump (G1311A), autosampler (G1329A), thermostat (G1316A), diode array detector (G1315D) set at 210 nm and refractive index detector (G1362A). An Alltech OA-1000 Organic Acid Column (9 µm 300 x 6.5 mm) plus guard column was used with 0.01 N H₂SO₄ as the eluent and the column was heated to 70 °C. A 10 µL injection volume obtained using a sample loop was used with a flow of 0.5 mL min⁻¹ over a measuring time of 20 min. Data obtained was analysed using Agilent ChemStation Software on a PC. Analysis runs lasted 30 minutes and a table showing the detector response factors and individual retention times is shown in Supplementary information (Table S1).

3 Results and Discussion

Elemental analysis showed the catalytic Au/TiO₂ material contained 0.9% Au. XPS revealed the Au was present in the zero valent state (with peaks in the 4f region at 83.6 and 87.3 eV). UV Vis spectroscopy showed an Au Plasmonic band centred at 550 nm (confirming nanoparticulate Au) and TEM showed the material had Au particles of ~ 5 nm (+/- 1.7 nm, n = 200). BET analysis revealed a surface area of 51 m²g⁻¹. Typical XPS and UV-vis spectra, as well as TEM micrographs and BET plots are shown in the supplementary information section (Figures S1 – S4).

Previous publications [27] have shown that the reactivity and selectivity of supported Au catalysts varies as a function of pH. In these reactions we are limited by the pH attainable through the partial dissolution and suspension of group II oxides in aqueous systems and the reactions were held at pH values of between 11.7 and 11.8. In order to achieve these pH values, 5 x 10⁻³ moles of NaOH and BaO were added to the reaction solution while 1 x 10⁻² moles of CaO were required.

Regarding catalytic reactivity, significant portions of the solid bases dissolved during the reaction. Following the 4h experiments the solution contained 2000 ppm dissolved Ba (~ 29% of the BaO) and 1300 ppm of dissolved Ca (~32% of CaO). In preliminary experiments it was shown that neither material (CaO or BaO) promoted the reaction in the absence of deposited Au. Hutchings *et al.* [25] have noted glycerol conversion when using un-promoted MgO as a catalyst (at levels of 0.8% conversion following 4h reaction under 300 kPa O₂).

Figure 2.

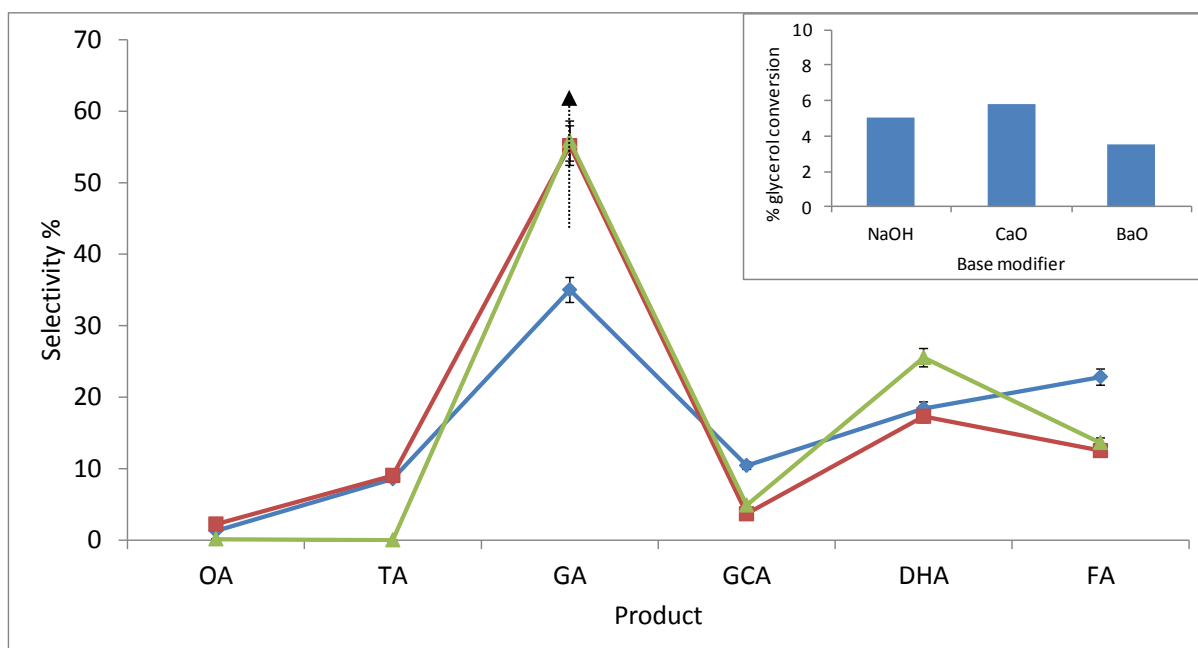


Figure 2. Reactivity and product distribution following 4h oxidation experiments at 60 °C over Au/TiO₂ catalysts using NaOH (◆), CaO (▲) and BaO (■) to adjust pH (to 11.7 - 11.8) Key: OA – Oxalic acid, TA – Tartronic acid, GA – Glyceric acid, GCA – Glycolic acid, DHA – Dihydroxyacetone, FA – Formic acid. The inset shows the % glycerol converted during these reactions and the dotted arrow highlights the increased selectivity to GA.

Figure 2 shows the product distributions from typical 4 h glycerol selective oxidation experiments over the 1% Au/TiO₂ catalysts where the reactions are differentiated according to the basic materials used to adjust the pH to the range mentioned above. The inset shows the overall glycerol conversion in each case. The conversions of glycerol were between 3.5% (when BaO was used as a base) and 5.8% (when CaO was used as a base). When NaOH(aq) was used the conversion was intermediate at 5.0%. While these conversions are relatively low, it should be recalled that the conditions of temperature and pressure that we are using are not

forceful (60 °C and atmospheric pressure). It would be expected that conversion would increase at higher temperatures under pressures of O₂.

In all cases dihydroxyacetone, glyceric acid and formic acid were the principal products formed with relatively small amounts of tartronic and glycolic acids produced. There is also a minor production of oxalic acid. There is clear selectivity changes between the reactions where the aqueous base is used compared to those where the two suspensions were used, the main change being that the selectivity towards glyceric acid is increased in the presence of the suspensions.

This increase, see figure 2, involves a change from 35% of the product collected to 56% at the expense of the production of glycolic (GCA) and formic acids (FA), *i.e.* products of C-C bond cleavage. Given that the latter products (FA and GCA) are formed from oxidation and cleavage of the former (GA), it seems that the alkaline earth oxides play some role in stabilizing glyceric acid against further oxidation.

Another difference in the CaO modified reaction compared to the standard NaOH(aq) modified solution is the slightly increased production of dihydroxyacetone and the absence of tartronic acid in the product mixture.

The effects of changing the amount of CaO within the reaction mixture were also studied (see figure 3). In this series of reactions, the CaO / glycerol ratio was

adjusted to values of 0.05, 0.2 and 1. This led to an increase in the initial pH of the reaction mixtures (11.7 to 11.8 to 11.9) and also led to an increase in glycerol conversion over the Au/TiO₂ catalyst (6.3%, 6.8% and 9.1%). Interestingly the reaction selectivity did not appreciably change with pH. This is in contrast to the situations where NaOH is used to alter pH [27].

Figure 3.

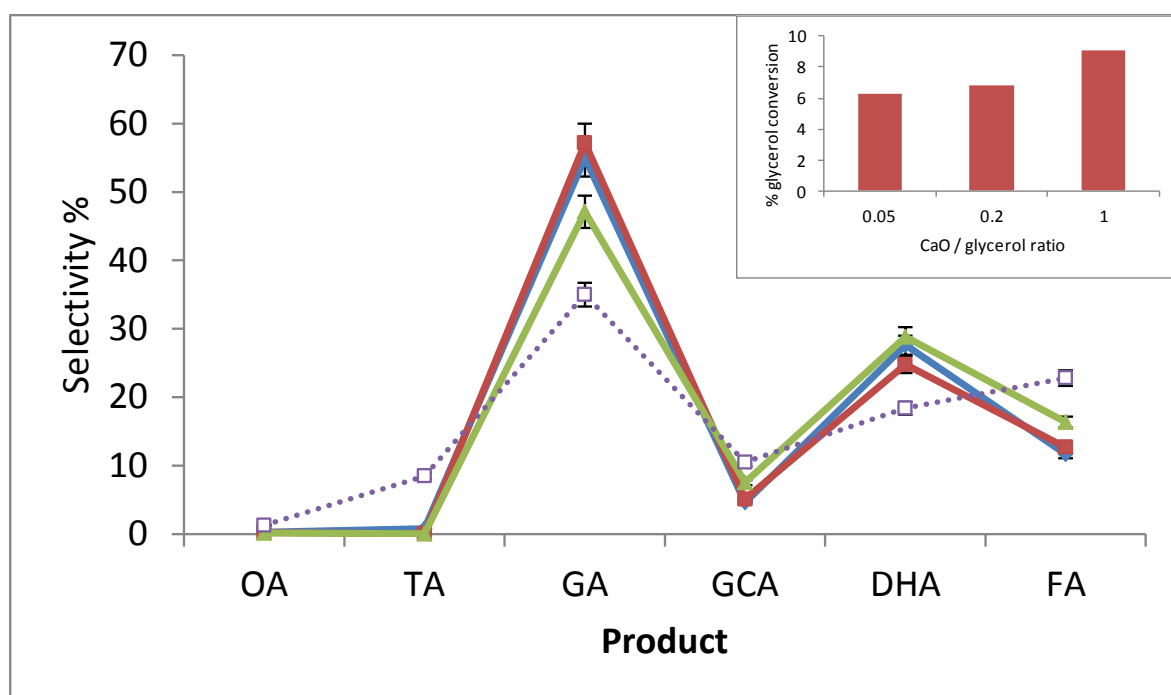


Figure 3. Product distribution following 4h oxidation experiments at 60 °C over Au/TiO₂ catalysts using CaO with different CaO/glycerol molar ratios, 0.05 (■), 0.2 (◆) and 1 (▲) Key: OA – Oxalic acid, TA – Tartronic acid, GA – Glyceric acid, GCA – Glycolic acid, DHA – Dihydroxyacetone, FA – Formic acid. This inset shows the % conversion of glycerol in each case and the dotted line shows the selectivities when NaOH(aq) is used.

The two solid bases were also used as supports for Au nanoparticles in order to determine whether the materials could act as base modifiers while also acting as

catalyst supports. Preparation of these catalysts using the deposition precipitation technique was not straightforward (presumably due to pH effects on the precipitation), and the final materials generated were a 0.2% Au/CaO catalyst and a 2.4% Au/BaO material. The former had Au particle sizes of 3.4 (+/- 1.2 nm, n=200). No TEM images showing Au particles on BaO could be collected but in any case this material showed no activity for the promotion of the oxidation reaction.

Figure 4

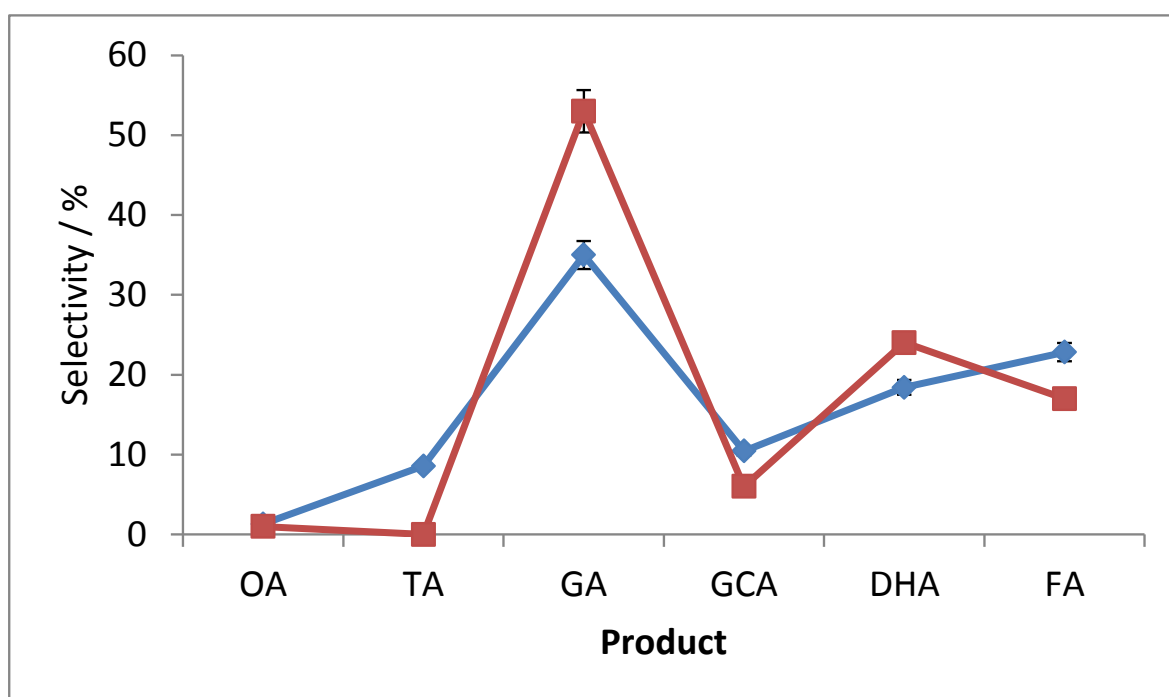


Figure 4. Product distribution following 4h oxidation experiments at 60 °C over Au/TiO₂ using NaOH as a pH modifier (◆) and Au/CaO (with no additional pH modifier) (■) catalysts, Key: OA – Oxalic acid, TA – Tartronic acid, GA – Glyceric acid, GCA – Glycolic acid, DHA – Dihydroxyacetone, FA – Formic acid.

In contrast, the Au/CaO (0.2% Au) and Au/TiO₂ (1% Au) / NaOH reaction systems both gave comparable conversions of glycerol. Again, in the case of the Au/CaO material ~ 14% of the CaO dissolved in the reaction medium (leading to a measurable concentration of ~ 380 ppm Ca). Figure 4 shows the selectivity of the

reactions over both reaction systems and it is clear that in the presence of NaOH the selectivity to glyceric acid is decreased.

In a final set of experiments the dissolved fraction of the CaO from one of these experiments was used as the base modifier (*i.e.* no solid phase CaO was present) in the presence of a fresh sample of the model Au/TiO₂ catalyst. Once again the reaction was far more selective for the production of Glyceric Acid (GA) than was the case when dissolved NaOH was used as the base modifier (*i.e.* 52% selectivity compared to 35% at similar conversions).

Therefore, in all cases where CaO (or BaO) are used to modify the pH of the reaction it seems that the presence of dissolved M²⁺ stabilizes glyceric acid against further oxidation and C-C bond cleavage (when compared to the situation where NaOH(aq) is used – see figure 2). This obvious change in selectivity may involve a coordination of the anion of glyceric acid with the Ca²⁺ or Ba²⁺ ions in solution. One substance that might be responsible for this stabilization is glyceric acid hemicalcium (CAS Number 207300-72-9) or a Ba²⁺ analogue, *i.e.* it is possible that this salt (see figure 1) forms following interaction between formed deprotonated glyceric acid and dissolved Ca²⁺ ions and that this stabilizes the GA against further oxidation to GCA and FA.

4 Conclusions

We have shown that alkaline earth oxide solid phase materials can adjust the pH of a glycerol oxidation reaction in the presence of a nanoparticulate Au catalyst.

Glycerol conversions are of the same magnitude as when aqueous bases are used but the reaction selectivity is altered.

This alteration is manifest by decreased production of 1 and 2 C fragments produced from the oxidation of glyceric acid in the presence of solid bases and we suggest that dissolved group II ions play some role in stabilizing glyceric acid against further oxidation, possibly through the formation of stable coordination complexes in solution.

Acknowledgements

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Supplementary information for

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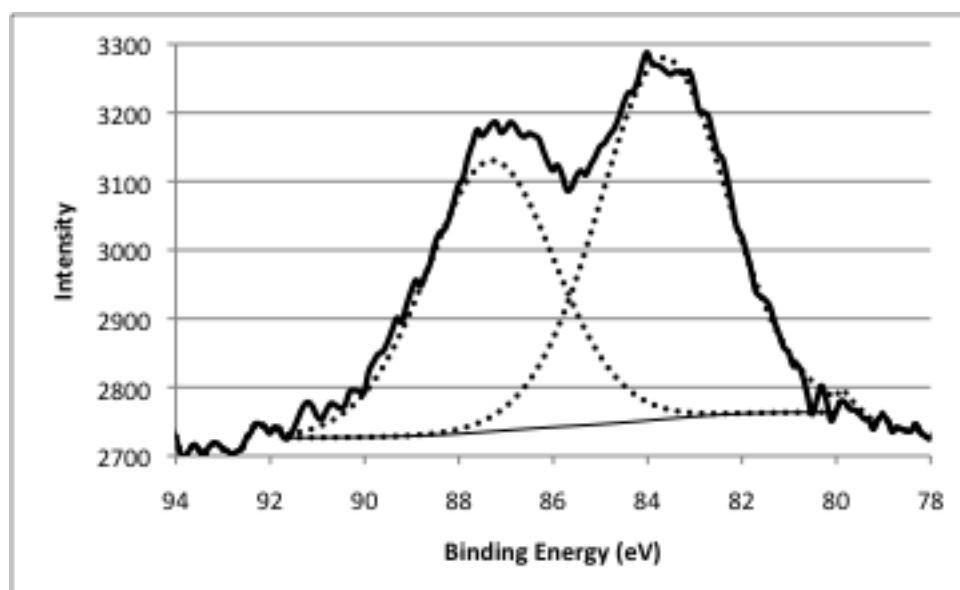


Fig S1 Typical XPS Au 4f spectrum of calcined Au/TiO₂.

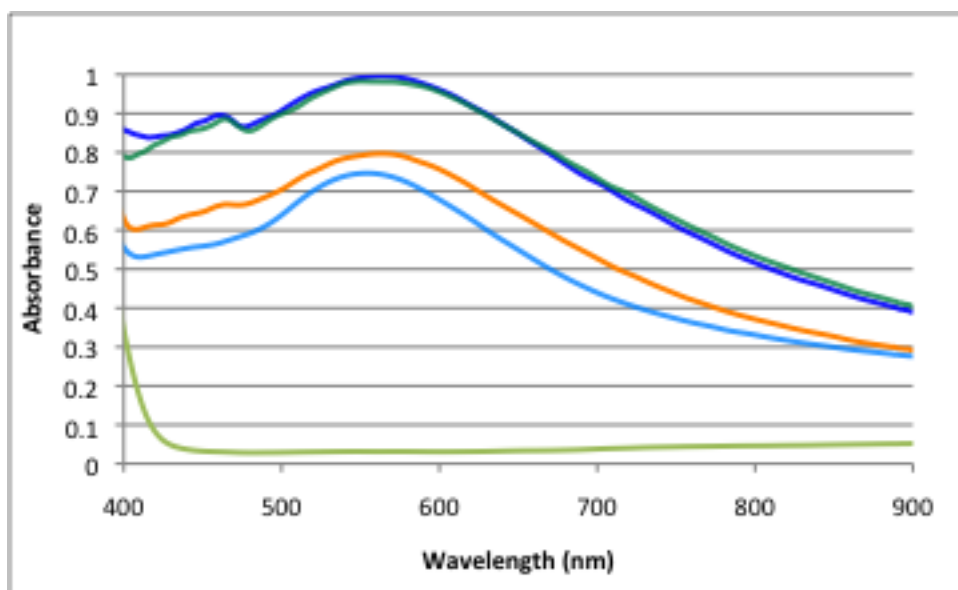


Figure S2. UV-Vis spectra of Au/TiO₂ samples prepared using the urea deposition method. Key: ■ TiO₂ support, and various Au/TiO₂ samples ■, ■, ■, ■.

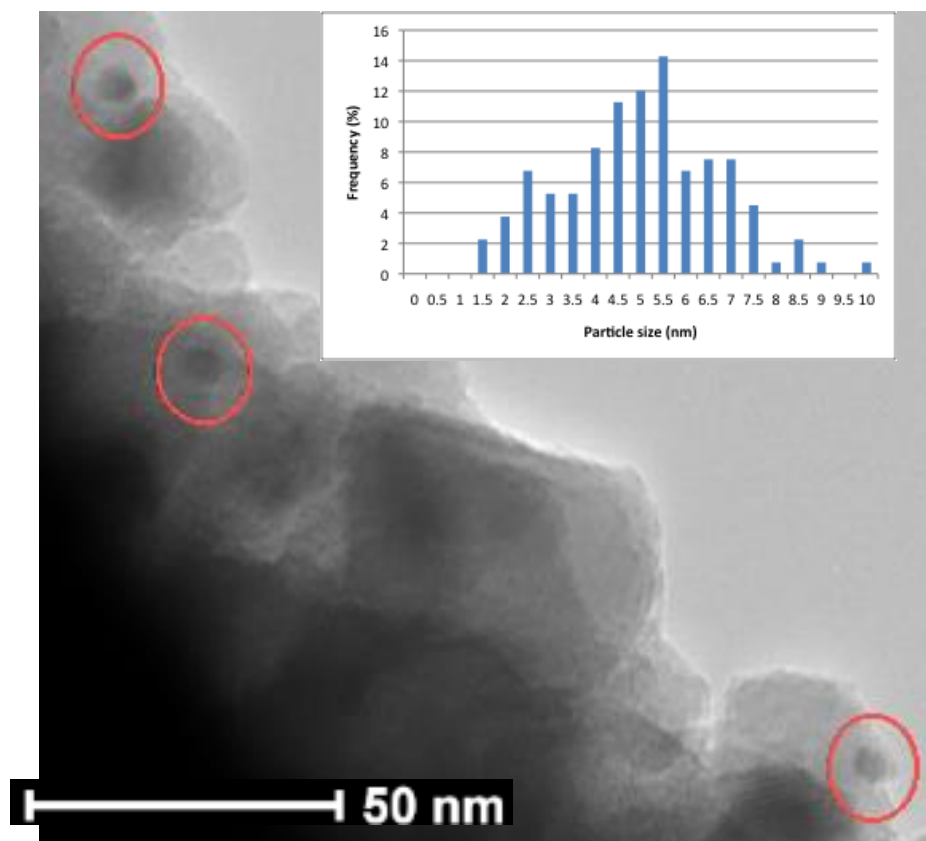
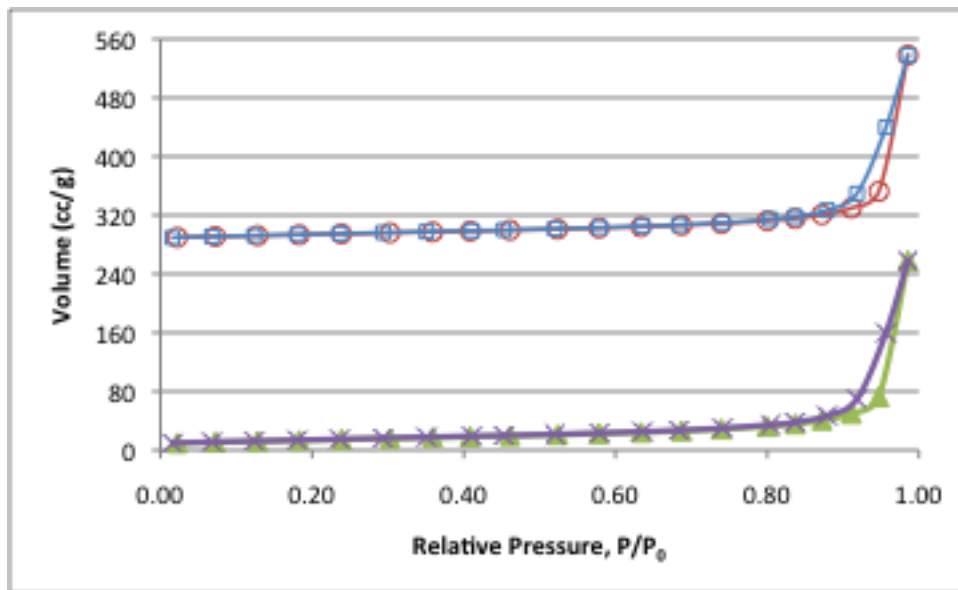


Figure S3. Typical TEM image of Au/TiO₂. Inset contains particle size distribution.



S4. Displaced full nitrogen physisorption isotherms of the TiO₂ support (upper plots) and Au/TiO₂ (lower plots)

Table S1. Calibration factors obtained from the slopes of calibration plots of concentration against peak area for each of the compounds investigated.

Detector:	Retention time / min.	Response Factor	
		DAD	RID
		(mAU mM ⁻¹)	(nRIU mM ⁻¹)
Acetic acid	15.8	40.81	5.318 x10 ³
Dihydroxyacetone	12.5	48.44	1.252 x10 ⁴
Formic acid	8.5	44.78	2.592 x10 ³
DL-Glyceraldehyde	10.7	28.93	1.527 x10 ⁴
DL-Glyceric acid	10.3	67.51	1.123 x10 ⁴
Glycerol	12.5	N/A	1.353 x10 ⁴
Glycolic acid	11.4	51.73	8.618 x10 ³
Glyoxylic acid	9.1	68.04	1.088 x10 ⁴
β-Hydroxypyruvic acid	7.9	385.3	1.264 x10 ⁴
Oxalic acid	6.2	1317	1.423 x10 ⁴
Tartronic acid	7.6	340.2	1.779 x10 ⁴