The selective oxidation of glycerol over model Au/TiO_2 catalysts – the influence of glycerol purity on conversion and product selectivity.

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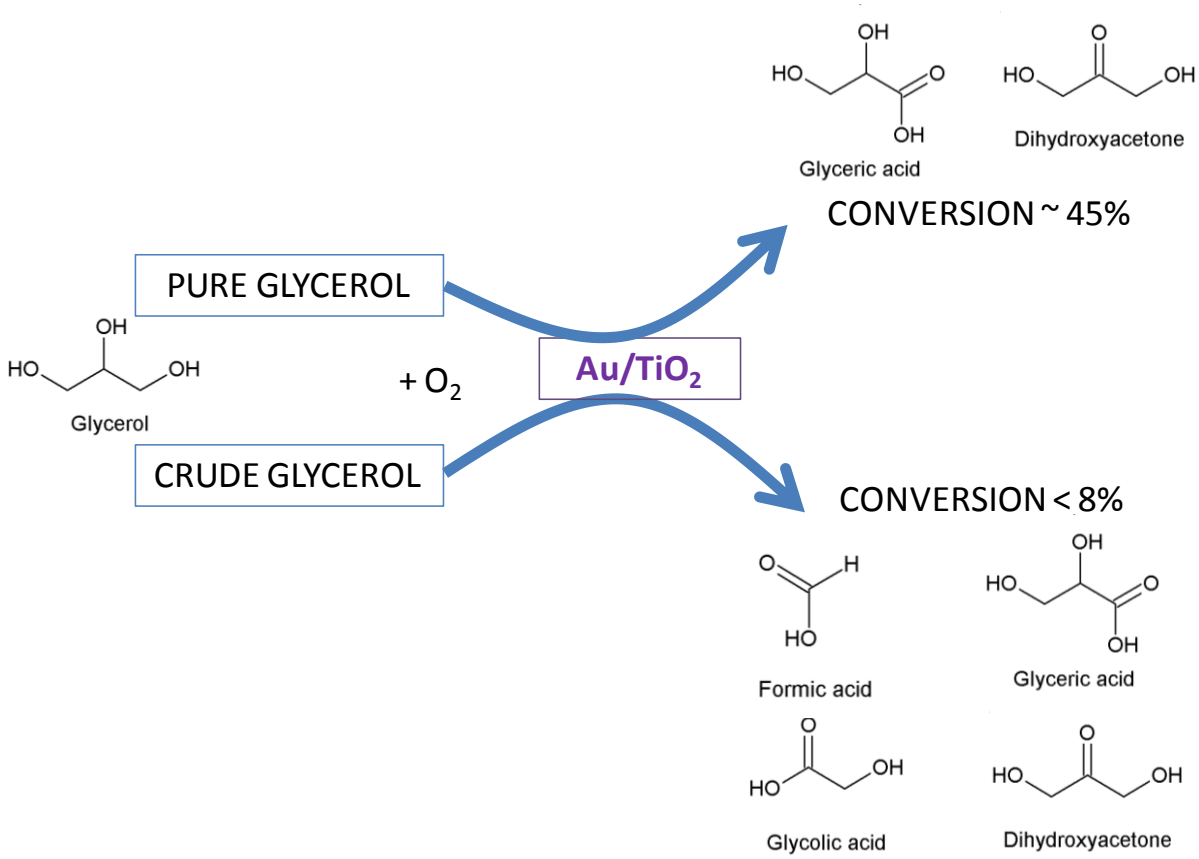

- Au/TiO_2 is a relatively active catalyst for pure glycerol oxidation
- Activity and selectivity change as crude glycerol is used
- The catalyst is poisoned by impurities in the crude substrate
- Ion-exchange and esterification of the crude substrate ameliorate this somewhat.

Abstract

The activity and selectivity of a model Au/TiO_2 catalyst was studied in the selective oxidation of glycerol as a function of the purity of the glycerol source. A reasonable conversion was noted when reagent grade starting materials were used. When crude glycerol from a FAME production facility was used, the activity of the catalyst was severely compromised and the selectivity of the reaction changed. Several low-cost approaches to purifying the crude glycerol were attempted but none resulted in the formation of a glycerol substrate whose conversion under reaction conditions matched that of the pure reagent grade substrate.

Keywords: glycerol oxidation, biorefinery, catalyst

1.0 Introduction.

As a by-product formed in large volumes from the transesterification of triglycerides in the formation of Fatty Acid Methyl Esters (FAME) biodiesel, glycerol has recently begun to attract attention as a potentially attractive starting material in a range of transformations. [1-3]

Its valorisation through selective oxidation [5], etherification [6], dehydration [7] or reformation to H_2 [8] would impact on the economics of FAME production and further improve the atom efficiency (and carbon balance) of biodiesel production from vegetable or animal derived triglycerides.

Because of this, there has been significant recent research effort involved in developing catalysts for the selective transformation of glycerol (through oxidation with O_2) into value added products such as dihydroxyacetone, glyceric acid, glycolic acid, oxalic acid *etc*. [8-15]

One of the principally studied catalytic materials to promote such selective oxidation reactions using molecular O_2 are supported Au nanoparticles and there is a relatively large body of work showing the selective oxidation of glycerol over these [13-19].

Normally in these research efforts the glycerol source studied has been of a commercial reagent grade with purities reported of > 98% [20].

On the other hand, glycerol produced during the transesterification process is invariably impure, containing a range of other materials, including mono and di-substituted triglycerides, free fatty acids (FFA), methanol, salts from catalyst residue (KOH) and, phosphoric acid (used during neutralisation), methyl esters, and other organic material (depending on the purity of the triglyceride source used in FAME production) [21-22]. In general, purification of this is a time consuming and expensive process involving vacuum distillation, electro-dialysis, nano-filtration and ion exchange steps [1, 21-22]. Ideally, for its eventual use in any integrated bio-refining process, it should be processable to the desired value added product from this impure state.

There is a drive to develop catalysts and transformations that will eventually form components of integrated bio-refining processes, and in general while reactions over model catalytic systems are useful in providing lead materials for future development and give valuable information about reaction mechanisms *etc*., any material that will find a commercial application in a biorefining application will need to operate using crude

substrates [23]. This is particularly true because of the differences between biomass and petrochemical derived feedstocks in terms of relative purity and homogeneity

There have been several attempts (with varying levels of success) to use crude glycerol as a substrate in many catalysed transformations and direct uses of glycerol including the direct glycerol fuel cell [24, 25] dehydration to form acrolein [26, 27], photo-oxidation [28] and reforming [29]. There have also been attempts at biochemical transformations [30].

In this work we compare the activity and selectivity of a model Au/TiO_2 catalyst in the glycerol + O_2 reaction (under atmospheric pressure) using pure and crude glycerol. We also present several low-cost techniques for purifying the crude substrate and report the effects of these treatments on reactivity over the model catalyst. Of direct relevance to this work, Gil *et al.* [31] have studied the selective oxidation over a range of Au/C catalysts and noted that the activities of these catalysts in promoting the reaction were unaffected by the nature of the glycerol source (albeit after neutralisation and evaporation steps). These results differ markedly from those we record over analogous Au/TiO_2 catalysts (showing that these catalysts are far more sensitive to substrate purity).

2.0 Experimental

2.1 Catalyst Preparation TiO_2 (Degussa P25) was pre-densified before use by wetting with deionised water followed by calcination at 550 ˚C for 2 h. Subsequently, the material was ground using a pestle and mortar and a 1% Au/TiO_2 catalyst was prepared using a standard deposition precipitation procedure [32].

20 mL of an aqueous solution of $HAuCl_4.3H_2O$ (ACS reagent, Sigma-Aldrich) (5.08 $x10^{-5}$ mol) was added to 20 mL of an aqueous solution of urea (99 +% ACS reagent) (0.61 g, 1.02 $x10^{-2}$ mol,) and heated to 80 ˚C with stirring. This resulted in the formation of a clear yellow solution. Sodium citrate (5.08 x 10^{-5} mol) and TiO_2 (1 g) were 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 $AgNO_3$ test), dried at 80 ˚C for 2 h and activated by calcination in static air at 300 ˚C for 4 h.

2.2 Au/TiO_2 Characterisation The Au/TiO_2 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) and BET analysis (NOVA 2200e Surface Area and Pore Analyser, Quantachrome Instruments).

2.3 Catalytic reactions Catalytic reactions were carried out in a semi-batch process at atmospheric pressure within 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 24 hours under atmospheric pressure using a flow of air (10 mL min^{-1}), delivered into the solution through the sparge. The solution was stirred at a rate of 600 rpm. Aqueous glycerol (0.3-0.5 M, 100 mL) in 1M NaOH 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 H_2SO_4).

Products were analysed using HPLC on an Agilent Technologies 1200 series HPLC equipped with a degasser (G1322A), quaternary pump (G1311A), autosampler (G1329A), thermostat (G1316A), diode array detector (G1315D) set to 210 nm and refractive index detector (G1362A). An Alltech OA-1000 Organic Acid Column (9 µm 300 x 6.5 mm, 70 °C) plus guard column was used with 0.01 N H_2SO_4 as the eluent. 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.

2.4 Materials Pure glycerol was obtained from sigma Aldrich (Sigma Ultra >99% GC). Crude glycerol was obtained from Green Biofuels Ireland Ltd. (Marshmeadows, New Ross, Co. Wexford) [33]. Triglyceride starting materials in their biodiesel synthesis process were obtained from a range of sources including meat processors, food processing factories and large restaurant chains – meaning that a relatively heterogeneous range of triglycerides were used.

NaY (SiO_2/Al_2O_3) = 4.1 and hydrotalcites ($Mg_6Al_2(CO_3)(OH)_{16}.4H_2O$ were purchased from Alfa Aesar and Aldrich respectively. Before use, the crude glycerol was filtered through 11 µm cellulose filters (Whatman Grade 1) to remove suspended particles.

2.5 Attempts to purify crude glycerol Two attempts were made to further purify the crude glycerol. The aim of these attempts was to provide an inexpensive and easily implemented method of purification. These were, firstly, an ion-exchange treatment and secondly, a pre-esterification step.

The ion exchange step involved 0.5 g of NaY-Zeolite and 0.5 g hydrotalcite being added to 10 mL filtered crude glycerol and shaken for 4 h, followed by filtration using 11 µm cellulose filters (Whatman Grade 1).

The pre-esterification step was carried out as follows. 10 mL (5.00×10^{-5} mol) 0.01 N H_2SO_4 and 10 mL (2.47×10^{-4} mol) methanol were added to 20 mL filtered crude glycerol and stirred at 400 rpm at 60 ˚C with a reflux condenser for 2 h. Following this, the mixture was left to settle and separate. Finally the lighter aqueous phase was decanted from dense organic phase. Other workers using similar processes have reported over 97% removal of FFA from seed oil mixtures [34].

3.0 Results and discussion

The standard Au/TiO_2 catalyst was characterised using a range of techniques. Elemental analysis showed it contained 0.9% Au while XPS revealed this 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 (suggesting nanoparticulate Au) and TEM confirmed this with Au particles of ~ 5 nm (+/- 1.7 nm, n = 200) being visible. BET analysis yielded a surface area of 51 m^2g^{-1}.

The crude glycerol was analysed using a range of techniques. HPLC showed it to be 68.5% glycerol while elemental analysis showed sulphur (2.5%), phosphorous (0.2%), potassium (3.4%) and sodium (0.1%) with Karl Fischer titration giving a water concentration of ~18.8%. The pH of the crude material was 5.5 (that of pure glycerol being 6.1). This acidity could arise from overuse of the neutralising acid used in the biodiesel production process, or from

the presence of free fatty acids (FFA) in the mixture. Titration with NaOH gave an acid concentration of 2.3 x 10^{-4} M which suggests that the bulk of the acidity arises from un-dissociated FFA.

Figure 1 shows the conversion of pure and crude glycerol to products following a 24 h reaction at 60 °C in a flow of air over 394 mg of the model Au/TiO_2 catalyst. It should be noted that these conversions are from a reaction under atmospheric pressure (rather than under a pressure of O_2. In all cases the conversion of glycerol increased linearly from t = 0 to t = 24h.

Figure 1

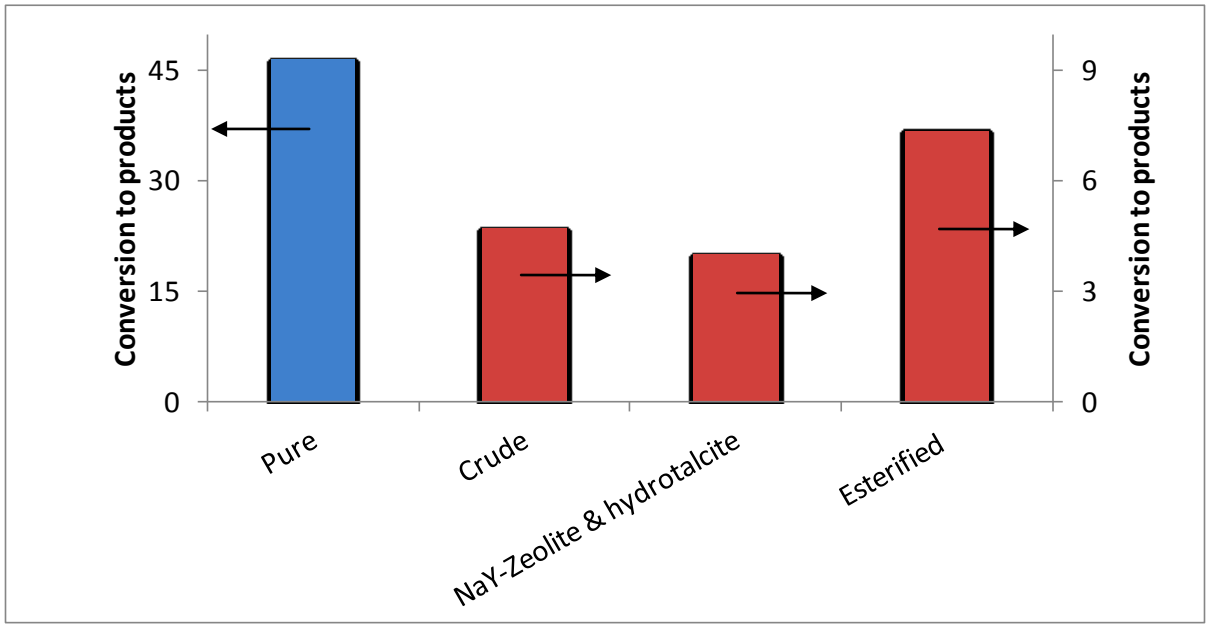

Figure 1. Conversion to products for pure and crude glycerol substrates. Experiments (24 h) carried out using ~ 0.3 to 0.5 M glycerol (100 mL), T = 60 °C, under a flow of air (10 mL min^{-1}), 394 mg Au/TiO_2, 1 M NaOH, with constant stirring.

Post reaction characterisation of the catalysts using the techniques listed above showed no major differences between the post-reaction catalysts used in the pure or crude reaction

mixtures. However, FTIR and TGA has shown that hydro-carbonaceous material is adsorbed onto the catalysts during the reaction. FTIR cannot discriminate between these adsorbed species while TGA suggests and that the nature of this differs as a function of the purity of the substrate (see Supplementary Information S1 and S2). Any further analysis of the modes of deactivation (other than it may be related to the formation of an ad layer on the surface of the catalysts) is beyond the scope of the current communication.

The conversions following minor treatments in attempts to remove materials in the crude mixture are also shown.

These treatments involved (a) an ion-exchange process (where the material was shaken with an amount of NaY and hydrotalcites to remove K^+ and SO_4^{2-} / PO_3^{3-} respectively (replacing them with Na^+ and CO_3^{2-}) and (b) an esterification step where CH_3OH and H_2SO_4 were added and the mixture treated at 60 °C for 2h. The purpose of the latter treatment was to remove any FFA in the mixture (using them to generate an organic phase of fatty acid methyl esters (FAME)). While this treatment did generate an organic layer (suggesting FAME had been produced) it did not affect the pH of the mixture.

The ion-exchange treatments did not affect the concentrations of dissolved sulphur-containing species (their concentrations remained ~2.6%) but it did affect the concentrations of K (decreasing from 3.3% to 2.9%) and P (decreasing from 0.2% to 0.1%).

It is clear that conversion using the pure material was significantly higher (~ 45% of glycerol converted over 24 h) than when the crude material was used (~4.7% conversion over the same time period). Treatments to remove K and P and FFA did not substantially change this

conversion (with the removal of ions actually causing the measured conversion to fall (to 4%) and the esterification step resulting in the conversion increasing to ~7.3%.

Figure 2

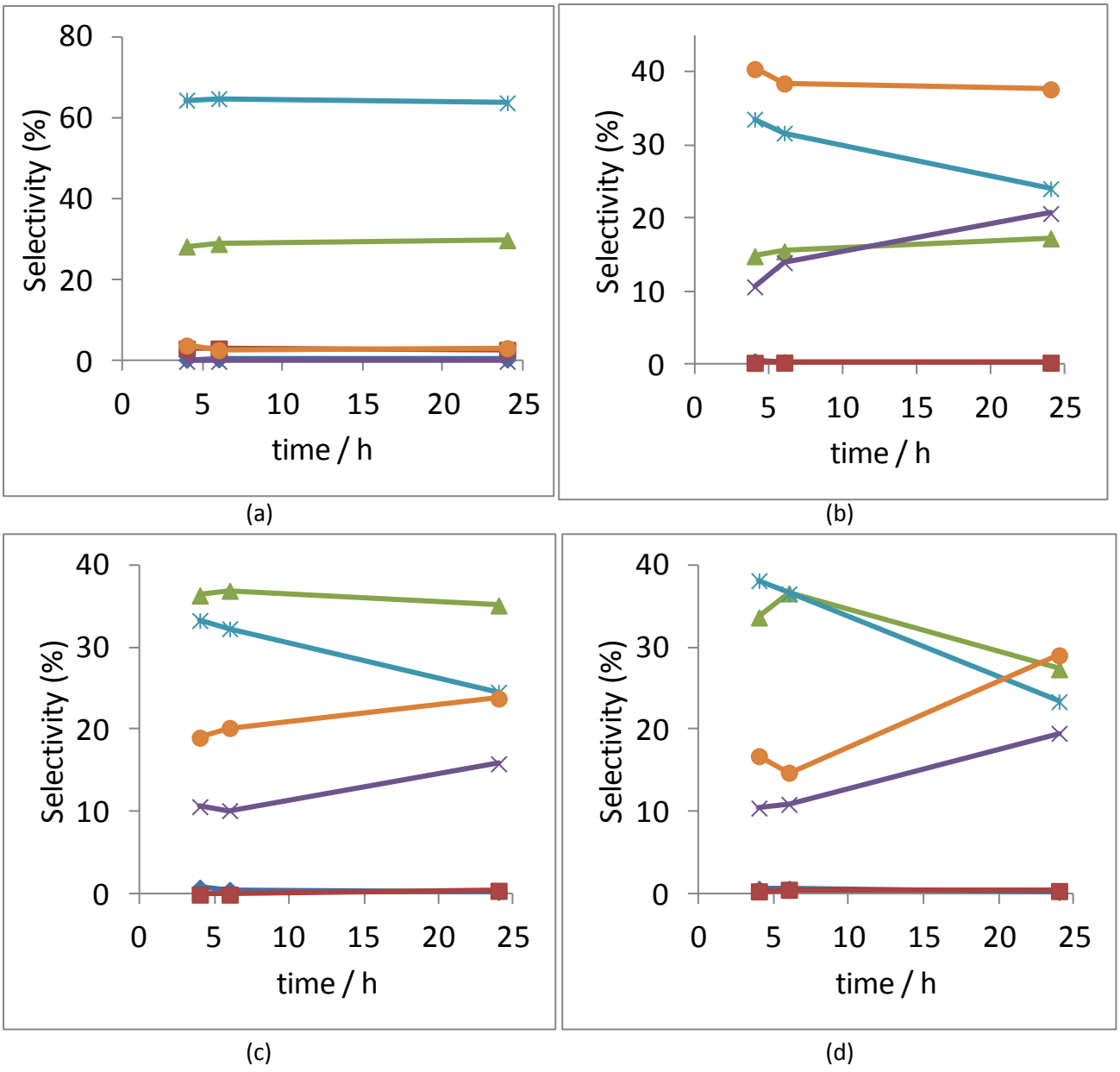

Figure 2: The liquid phase product distribution from the selective oxidation reactions detailed in figure 1 when the following are used as substrates; (a) pure glycerol (b) crude glycerol, (c) crude glycerol following an ion-exchange treatment and (d) crude glycerol following an esterification treatment. Dihydroxyacetone (✳), Glyceric Acid (▲), Tartronic Acid (■), Oxalic Acid (◆), Glycolic Acid (✕), Formic Acid (●).

Figure 2 (a) – (d) shows the different selectivities to product of the reaction over each of the glycerol substrates as a function of time, with reaction aliquots being extracted and analysed after 4, 6 and 24 h. of reaction.

The first aspect worth noting is that in the case of the reaction using the pure glycerol the selectivity is essentially unchanged over time. This shows that the catalytic reaction is unaffected by the time exposed to the reactants and products of the reaction.

Over this catalyst, dihydroxyacetone (following oxidation of the 2° alcohol group) was the main product (~64%) with significant amounts of glyceric acid (following oxidation of a 1° alcohol) (~29%) also being formed. Other products which arise from subsequent oxidation of glyceric acid are also formed (oxalic and formic acids and very minor amounts of tartronic acid). Interestingly no glycolic acid is formed even though it is reported that the main route of formation of formic acid is through the reverse aldol condensation of glyceric acid which should form equimolar concentrations of glycolic and (eventually *via* formaldehyde) formic acid [8].

When crude glycerol (and the two treated crude glycerol materials) were used as substrates the reactivity was significantly affected (see figure 1). But apart from this there was also a major effect on the selectivity of the reactions (see figures 2 (b), (c) and (d)). In all cases the selectivity was markedly different than when pure glycerol was used as the substrate and again in all cases the selectivity changed over the course of the reaction (indicating that the catalyst was affected by the reactants and products of the reaction).

In all cases there are now four main products, dihydroxyacetone, formic acid, glyceric and glycolic acids. Furthermore, in all cases selectivity towards the production of

dihydroxyacetone falls during the course of the reaction. Tartronic and oxalic acids (which were minor products when pure glycerol was used as a starting material) were detected here at extremely low levels (and recall these selectivities are from reactions where the overall conversion is extremely low). However glycolic acid is seen in all situations where a crude glycerol substrate is used.

Formic acid is the major product when crude glycerol is used and, while not being the major product in the reactions using the two treated glycerol substrates, selectivity to its formation (along with that of glycolic acid) increases over the 24 h period of the reaction.

The molar ratios of glycolic acid and formic acid resulting for these reactions are not those that would be expected (*i.e.* equimolar) if it were assumed that they were both formed form the reverse aldol fragmentation of glyceric acid [8]. This suggests some other mechanism of formation of formic acid.

The two treatments change the selectivity somewhat (recall that the first treatment removed a certain amount of K and P from the substrate, while the second removed un-reacted glycerides and FFA). In both cases this decreased the initial concentrations of formic acid formed (making glyceric acid the principal product of the reaction). The changing selectivity of the reaction with time suggests poisoning of the catalyst within the reaction mixture.

4.0 Conclusions

We have shown that replacing a pure glycerol raw material with a crude substrate derived from a biodiesel processing installation where the triglyceride substrates were obtained from a range of sources including meat processors, food processing factories and large restaurant chains resulted in a relatively active Au/TiO_2 catalyst, in an oxidation reaction at atmospheric pressure, losing its activity. Furthermore the product distribution from the catalysed reaction was significantly changed when the crude substrate was used (dihydroxyacetone was replaced by formic acid as the principal product formed). The fact that this selectivity changed over time when crude glycerol was used suggests that the catalyst was becoming poisoned during the reaction.

Relatively facile techniques (*i.e.* cation and anion ion-exchange, the addition of an esterification step to remove FFA), used to remove different impurities did not restore the conversion to that seen when pure glycerol was used as a substrate.

These results suggest that Au/TiO_2 catalysts will not be viable materials for the promotion of this reaction without extensive and expensive purification of the substrate.

5.0 Acknowledgements

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Supplementary information for "The selective oxidation of glycerol over model Au/TiO_2 catalysts – the influence of glycerol purity on conversion and product selectivity", James A Sullivan and Sarah Burnham,

Figure S1

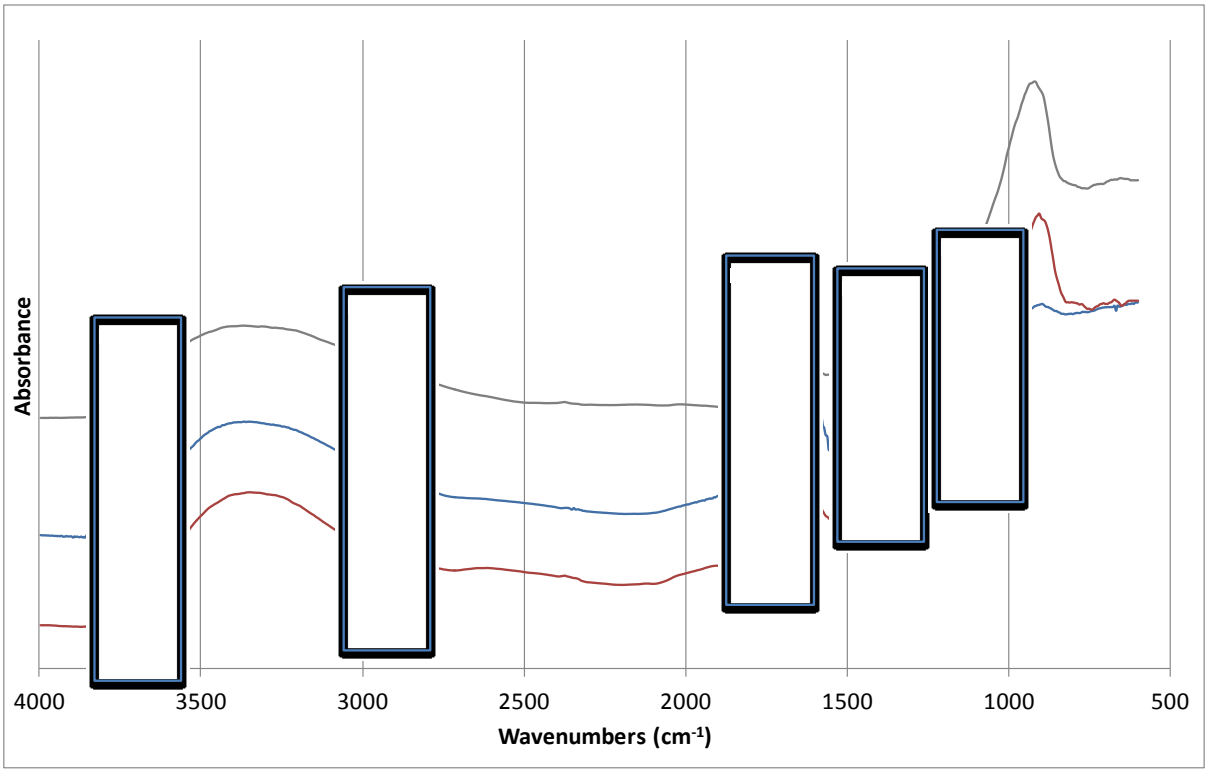

Figure S1 – FTIR spectra of the Au/TiO_2 catalyst before use (upper spectrum), and following use in pure (middle spectrum) and crude (lower spectrum) glycerol oxidation reactions.

Bands relating to CH vibrations are seen at ~ 2900 cm^{-1}, 1400 cm^{-1} and a band at 1100 cm^{-1} relates to a glycerol C-O stretch. The bands at ~ 1740 relates to a C=O functional group while the decrease of the band at 3700 cm^{-1} following contact with glycerol shows the surface OH interact with the substrates. There is no major difference in the spectra of the catalyst from the crude mixture when compared to that from the pure substrate.

Figure S2

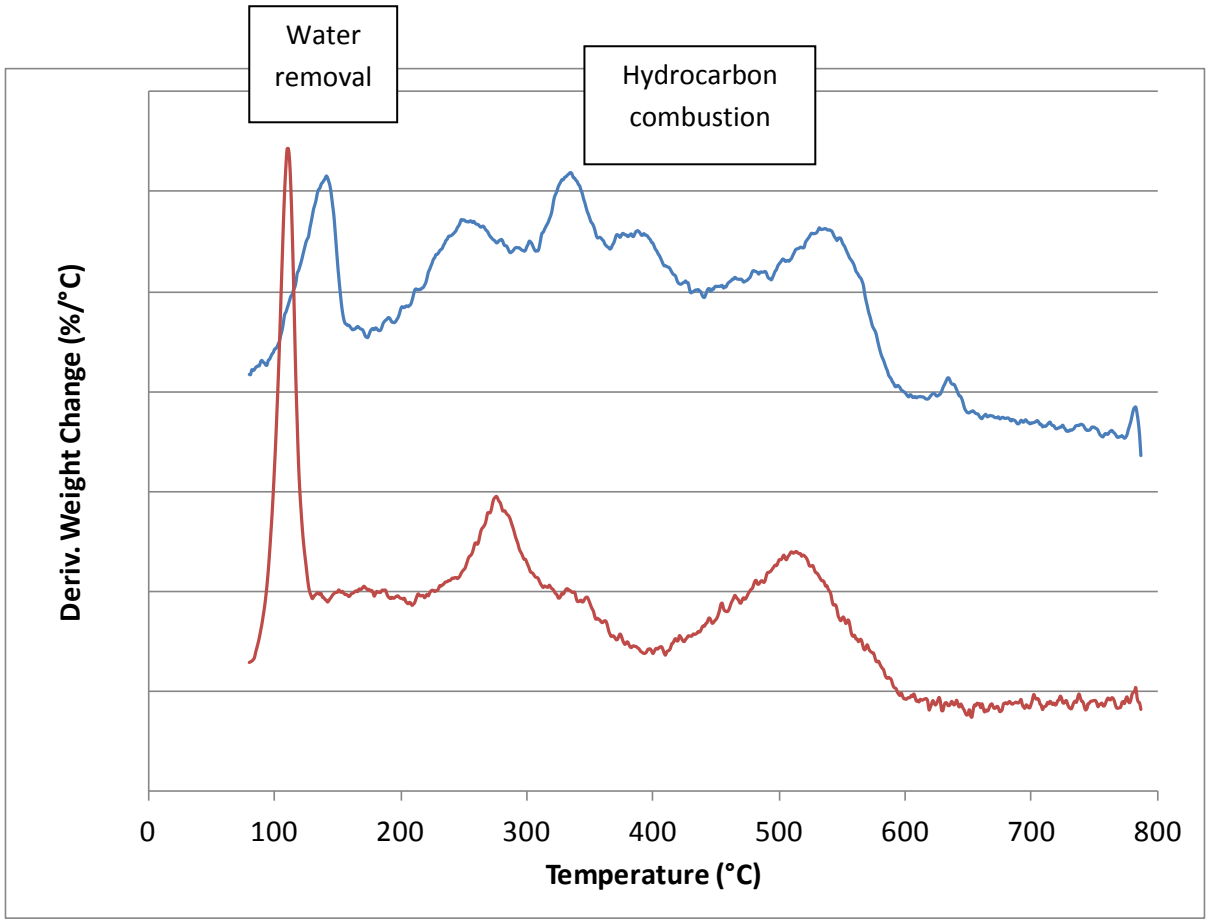

Figure S2 – TGA profiles of the post-reaction catalysts from the pure (upper profile) and crude (lower profile glycerol reaction mixtures. Lower temperature peaks relate to water removal while higher temperature peaks relate to the combustion of different types of hydro-carbonaceous deposits.

The ad layer from the “pure” reaction is less homogeneous than that from the “crude” reaction.