

Selective oxidation of glycerol to glyceric acid using a gold catalyst in aqueous sodium hydroxide

Silvio Carrettin,^a Paul McMorn,^a Peter Johnston,^b Ken Griffin^b and Graham J. Hutchings^{*a}

^a Department of Chemistry, Cardiff University, P.O. Box 912, Cardiff, UK CF10 3TB.

E-mail: hutch@cardiff.ac.uk

^b Johnson Matthey, Orchard Road, Royston, Herts, UK SG8 5HE

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Glycerol is oxidised to glyceric acid with 100% selectivity using either 1% Au/charcoal or 1% Au/graphite catalyst under mild reaction conditions (60 °C, 3 h, water as solvent).

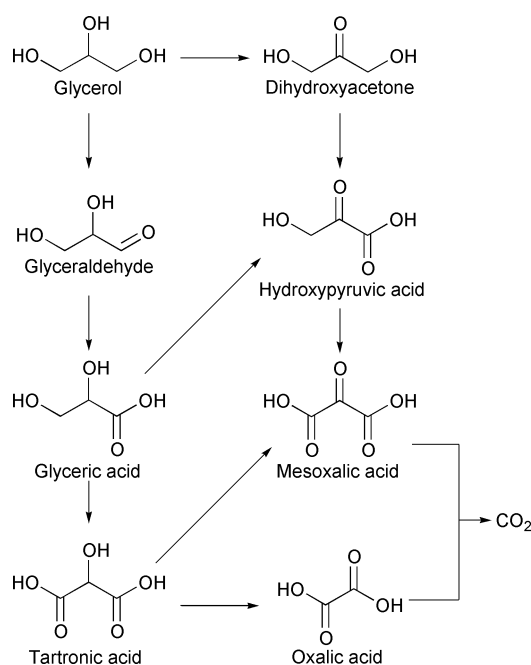
The identification of new catalysed reactions is of key importance to the chemical industry and, in particular, with respect to the production of fine chemicals. Selective oxidation is a key reaction used in the activation of raw materials to form useful products or chemical intermediates.¹ Glycerol is a highly functionalised molecule that is readily available from biosustainable sources, for example, it can be derived from rape seed and sunflower crops. A large number of products can be formed from glycerol oxidation (Scheme 1) and one of the key problems concerns the selectivity by which the individual products can be formed. However, if the products could be formed in high selectivity, they are potentially valuable as chemical intermediates in the fine chemicals industry. The oxidation of glycerol using supported Pd and Pt catalysts has been extensively studied by Kimura *et al.*^{2,3} and Gallezot and coworkers.^{4,5} In general, Pd as a catalyst was found to be more selective than Pt, and conditions were identified for which relatively high selectivities for dihydroxyacetone³ (70–80%) could be obtained, although it was found⁵ that dihydroxyacetone was readily converted to hydroxypyruvic acid at high conversions. Glyceraldehyde was also obtained in high selectivities⁴ (70–80%). However, it was noted that formic acid, probably resulting from the formation of oxalic acid, was also formed. In all these previous studies, mixtures of the possible products for glycerol oxidation (Scheme 1) have been observed. Recently, Prati and coworkers^{6–9} have shown that supported Au

catalysts can be selective for the oxidation of alcohols, including diols, under relatively mild conditions. We have now extended the study of gold catalysts and, in this communication, we show that glycerol can be oxidised to glyceric acid with 100% selectivity at high conversion.

1 wt% Gold catalysts supported on carbon and graphite were prepared as follows. The carbon support (graphite, or activated carbon, Johnson Matthey, 113.2 g) was stirred in deionised water (1 l) for 15 min. An aqueous solution of chloroauric acid (41.94% Au, Johnson Matthey, 2.38 g in 70 ml H₂O) was added slowly dropwise over a period of 30 min. The slurry was then refluxed for 30 min, cooled and reduced with formaldehyde over a period of 30 min. The slurry was refluxed for 30 min and, following cooling, the catalyst was recovered by filtration and washed with water until the washings contained no chloride. The catalyst was dried for 16 h at 106 °C. This method was also used to prepare 0.25 wt% Au/C and 0.5 wt% Au/C catalysts using smaller amounts of chloroauric acid.

The oxidation of glycerol with oxygen was investigated using the 1% Au/C catalysts in an autoclave¹⁰ and the results are given in Table 1. Water was used as solvent and sodium hydroxide was added as basic conditions are essential to obtain selective oxidation. Indeed, in the absence of sodium hydroxide, no glycerol conversion is observed. In addition, the carbon support in the absence of gold was also found to be inactive for glycerol oxidation, under these conditions, even when NaOH is present. The reaction products were analysed using HPLC.¹¹ For all the data presented in Table 1, the carbon mass balance was found to be 100%, and no C₂ or C₁ by-products were observed to be formed. In particular, it is apparent that the selectivity to glyceric acid and the conversion of glycerol are very dependent upon the glycerol/NaOH ratio. In general, with high concentration of NaOH, exceptionally high selectivities to glyceric acid can be observed. However, decreasing the concentration of glycerol, and increasing the mass of catalyst and the concentration of oxygen leads to the formation of some tartronic acid *via* consecutive oxidation. It is apparent that, by careful control of the reaction conditions, 100% selectivity to glyceric acid can be readily achieved. For comparison, the data obtained for a 5% Pt/activated carbon catalyst, similar to that used in previous studies,^{1–5} are also shown in Table 1. It is apparent that significant selectivities to glyceraldehyde or tartronic acid are observed with the Pt catalyst. We consider that the oxidation of glycerol to glyceric acid probably proceeds *via* initial formation of glyceraldehyde. Previous studies using Pt catalysts have confirmed that glyceraldehyde is rapidly oxidised to glyceric acid and is typically not observed as a product.^{12,13}

In a final set of experiments, the oxidation of glycerol and propane-1,2-diol was investigated using 0.25 wt% Au/graphite and 0.5 wt% Au/graphite catalysts, and the data are shown in Table 2. It is apparent that, for glycerol oxidation, both the selectivity to glyceric acid and the conversion of glycerol increase with the Au concentration. This is not observed for the oxidation of propane-1,2-diol, when the highest conversion is observed for the 0.5 wt% Au/graphite catalyst, although the selectivity to the monoacid does increase with increasing gold concentration. The previous studies by Prati and coworkers^{6–8} also show that reaction selectivity for alcohol oxidation is



Scheme 1

Table 1 Oxidation of glycerol using 1% Au/C catalysts^a

Catalyst	Glycerol/ mmol	pO ₂ /bar	Glycerol/metal mol ratio	NaOH mmol	Glycerol conversion (%)	Selectivity (%)		
						Glyceric acid	Glyceraldehyde	Tartronic acid
1% Au/activated carbon 12	12	3	538 ^b	12	56	100	0	0
1% Au/graphite	12	3	538 ^b	12	54	100	0	0
1% Au/graphite	12	6	538 ^b	12	72	86	2	12
1% Au/graphite	12	6	538 ^b	24	58	97	0	3
1% Au/graphite	6	3	540 ^c	12	56	93	0	7
1% Au/graphite	6	3	540 ^c	6	43	80	0	20
1% Au/graphite	6	3	214 ^d	6	59	63	0	12
1% Au/graphite	6	3	214 ^d	12	69	82	0	18
1% Au/graphite	6	6	214 ^d	6	58	67	0	33
1% Au/graphite	6	6	214 ^d	12	91	92	0	6
1% Au/graphite	6	6	214 ^d	0	0			
5% Pt/activated carbon	12	3	500	12	63	74	21	0
5% Pt/activated carbon	12	3	500	24	56	69	30	0
5% Pt/activated carbon	6	6	100	12	88	55	0	23

^a Reaction conditions: 60 °C, 3 h, H₂O (and 20 ml), stirring speed 1500 rpm; ^b 220 mg catalyst; ^c 217 mg catalyst; ^d 450 mg catalyst.

Table 2 Oxidation of glycerol using Au/carbon catalysts^a

Catalyst	Substrate	Conversion	Mono acid selectivity (%)
1 wt% Au/graphite	Glycerol	56	100
0.5 wt% Au/graphite	Glycerol	26	61
0.25 wt% Au/graphite	Glycerol	18	54
1 wt% Au/graphite	Propane-1,2-diol	32	100
0.5 wt% Au/graphite	Propane-1,2-diol	53	71
0.25 wt% Au/graphite	Propane-1,2-diol	28	65

^a Reaction conditions: 60 °C, 3 h, water 20 ml in an autoclave, stirring speed 1500 rpm, 12 mmol substrate, 12 mmol NaOH, 220 mg catalyst.

dependent upon the gold loading of the catalyst. This is most likely to be due to a particle size effect of the gold nanoparticles on the support. For gold, as an oxidation catalyst, it has been shown that the activity is highly dependent upon the particle size and, for CO oxidation, the optimum size is *ca.* 2–4 nm.¹⁴ However, the gold oxidation state, *i.e.* Au(III)/Au(0) ratio has also been found to be important in some cases.¹⁵ In the present study, both of these effects could be important and these will be the subject of a further study. The role of NaOH is worthy of further comment. It is proposed that, in the absence of base, the initial dehydrogenation *via* H-abstraction is not possible. In the presence of the base, the H is readily abstracted from one of the primary hydroxyl groups of glycerol and this overcomes the rate limiting step for the oxidation process. Hence, it is proposed that the oxidation mechanism proceeds *via* an initial dehydrogenation pathway as has been previously observed for other noble metal oxidation catalysts.¹⁶

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- The catalyst was suspended in a solution of glycerol in deionised water (20 ml) in a Parr autoclave (50 ml), the autoclave was pressurised to the required pressure with oxygen and heated to 60 °C. The reaction mixture was stirred (1500 rpm) for 3 h, following which the products were analysed by HPLC.
- Analysis was carried out using HPLC with ultraviolet (UV) and refractive index (RI) detectors. Reactant and products were separated on an ion exclusion column (Alltech OA-1000) heated at 70 °C. The eluent was a solution of H₂SO₄ (0.0004 M). Samples were taken at the end of the reactions, 10 µl of the sample was diluted in 100 µl of standard solution (isobutanol 0.2 M) and 20 µl of this solution was analysed.
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