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Oxidation of glycerol with hydrogen peroxide using silicalite and aluminophosphate catalysts

Paul McMorn[a,*], Glyn Roberts[b] and Graham J. Hutchings[a,*,**]

[a] *Leverhulme Centre for Innovative Catalysis, Department of Chemistry, University of Liverpool, Liverpool L69 3BX, UK*
[b] *Unilever Research and Engineering, Port Sunlight Laboratory, Quarry Road East, Bebington, Wirral L63 3JW, UK*

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The oxidation of glycerol using a range of metal-containing silicalite and aluminophosphate catalysts is described and discussed. Variation in reaction conditions (extent of conversion, temperature, glycerol/hydrogen peroxide ratio) or catalyst (silicalite containing Ti, V, Fe or AlPO-5 containing Cr, V, Mn, Co) did not lead to the formation of partial oxidation products of glycerol. Formic acid and a mono-formate ester of glycerol were observed to be the major products together with a complex mixture of acetals. Increasing the pore size of the catalyst was investigated for Ti-containing materials and it was found that increasing the pore size from ca. 0.5 nm for TS-1 to 15 nm for a titania–silica co-gel significantly increased the formation of partial oxidation products of glycerol, namely glyceraldehyde, dihydroxyacetone and glyceric acid.

Keywords: alcohol oxidation, hydrogen peroxide, TS-1, VS-1, glycerol oxidation

1. Introduction

Selective oxidation under mild reaction conditions has become a significant research topic since the discovery of the titanium silicalite TS-1 [1]. The oxidation of monohydric alcohols has been extensively studied with TS-1 [2–5] using hydrogen peroxide but, surprisingly, has been hardly studied with other related microporous and mesoporous materials. Van der Pol and van Hoof [3] studied a range of C_6–C_9 monohydric alcohols with the hydroxy group in the 1-, 2- or 3-position. They showed that the reactivity towards oxidation of the alcohol was determined by the position of the hydroxy group and the reactivity order was observed to be 2- $\gg$ 1- $>$ 3-alcohol. Subsequent studies by Maspero and Romano [4] and Hayashi et al. [5], using shorter chain alcohols, confirmed that alcohols substituted in the 2-position were the most reactive. Although monohydric alcohols have been well studied, diols and triols, e.g., glycerol, have not been investigated with TS-1 or related materials.

The oxidation of glycerol is of interest, since some of the selective oxidation products, e.g., glyceric acid and glyceraldehyde, are potentially useful as chemical intermediates. To date, there have been a number of studies of glycerol oxidation, but all have utilised carbon-supported Pt or Pd catalysts with molecular oxygen as oxidant [6–9]. Kimura et al. [6] showed that, by tuning the reaction conditions with these catalyts, selectivities to products such as dihydroxyacetone could be increased and that the reaction was pH sensitive. In particular, Bi promotion of Pt was found to significantly enhance the selectivity to dihydroxyacetone. Garcia et al. [7] studied glycerol oxidation using Pd/C catalysts and found that the selectivity to glyceraldehyde could be improved by increasing the pH with a maximum yield of 70% at 90% conversion at pH 11. However, over-oxidation to oxalic acid and carbon dioxide was also reported. Fordham et al. [9] also studied glycerol oxidation over bismuth-promoted Pd and Pt catalysts and showed that the oxidation of the primary hydroxyl group to give glyceric acid was dependent upon pH and that the oxidation of the secondary hydroxyl group of glyceric acid was preferred under acidic conditions.

In this paper, we report the study of the oxidation of glycerol using a range of transition-metal-containing silicates and aluminophosphate catalysts using hydrogen peroxide.

2. Experimental

2.1. Synthesis of TS-1

TS-1 was prepared by a method based on that of Tarramasso et al. [1]. Titanium(IV) ethoxide (0.36 g) was added slowly to tetraethylorthosilicate (10.4 g) and the resulting mixture was stirred for 2 h. The mixture was added slowly to tetrapropylammonium hydroxide (50 ml, 20% in water, Alfa) and heated (60 °C, 2 h), water being added to maintain the gel at constant volume. The gel was then aged (24 h) and heated (48 h, 175 °C) in a teflon-lined autoclave under autogeneous pressure. The solids were recovered by filtration and dried (100 °C) and calcined (air, 550 °C, 16 h) prior to use. Silicalite (S-1) was prepared in the same manner with the omission of the titanium(IV) ethoxide.

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[*] Present address: Department of Chemistry, Cardiff University, Cardiff CF10 3TB, UK.

[**] To whom correspondence should be addressed.

2.2. Synthesis of FeS-1

FeS-1 was prepared by a method based on the work of Szostak et al. [10,11]. Tetraethyl orthosilicate (10.4 g) was added to tetrapropylammonium hydroxide (50 ml, 20% in water) and stirred for 30 min. Iron(III) nitrate monohydrate (0.51 g) dissolved in water (1.7 g, distilled) was acidified with fuming nitric acid until a colourless solution was obtained. The two solutions were mixed (tetraethylorthosilicate/tetrapropylammonium hydroxide added with stirring to the iron nitrate solution) to form a lemon coloured gel which was heated (48 h, 165 °C). The solid was recovered by filtration, dried (100 °C) and calcined (4 h N_2, 4 h air, 550 °C).

2.3. Synthesis of VS-1

Tetraethylorthosilicate (10.4 g) was added slowly to tetrapropylammonium hydroxide (50 ml, 20% in water) and stirred for 30 min. Vanadyl sulphate (0.32 g) dissolved in water (1.7 g, distilled) was then added. The gel was then heated (72 h, 175 °C) and the solids recovered by filtration, dried (100 °C) and the blue/grey solid calcined (air, 16 h, 550 °C) to give a white solid.

2.4. Synthesis of transition metal aluminophosphates (MeAPO-5: Me = Cr, V, Co, Mn)

The synthesis was based on the method of Wilson and Flanigan [12]. Aluminium isopropoxide (20.4 g, Sigma) was stirred with water (20 g, distilled) and the two solutions were slowly mixed with stirring and the stirring was continued for a further 2 h. The transition metal compound (e.g., $VOSO_4$ 0.63 g, Cr_2O_3 0.38 g, $Co(NO_3)_2$ 0.73 g, $MnSO_4 \cdot 4H_2O$ 0.56 g) was then added and the mixture was stirred for 1 h. Tripropylamine (7.15 g, Fluka) was added with stirring and the gel was heated (16 h, 175 °C) and the solids were slurried with water and recovered after settling for several minutes. The water was removed by decantation and the procedure repeated until the wash water was clear. The solid was dried (100 °C) and calcined (16 h, 550 °C, air).

2.5. Oxidation of glycerol using hydrogen peroxide

Catalysts were tested under standard conditions and all materials were characterised prior to use using X-ray powder diffraction and infrared spectroscopy and were confirmed to have the required structures and crystallinity. In a typical reaction, glycerol (10 g) and catalyst (0.25 g) were stirred together at the required reaction temperature. Hydrogen peroxide was then added and samples for analysis were taken as the reaction proceeded. The analysis of the oxidation products of glycerol required derivatisation to the corresponding silyl ether using the following procedure based on the method of Smith and Carlsson [13]. The reaction products were reacted with an excess of hexamethyl disilazane and trimethylchlorosilane in pyridine. In this reaction, free alcohol groups are converted to silylethers. Water was added to dissolve the by-product of ammonium chloride and the upper organic layer was collected and analysed by gas chromatography (30 m DB-5 megabore column) and GC/MS.

3. Results

Initial experiments were carried out with TS-1 as catalyst using excess hydrogen peroxide (glycerol (5.0 g)) reacted with hydrogen peroxide (20 g, 70% w/v) in water (45 ml) at 80 °C. The results were quite surprising since none of the expected products were observed using GC analysis, even at very low conversion levels (e.g., 0.9% conversion after 2 h reaction). However, use of GC/MS analysis did show that very low traces of selective oxidation products were formed. Instead, formic acid, formate esters of glycerol, hydroxyethanoic acid and a complex mixture of acetals were observed. The complexity of the products required GC/MS for confirmation of their identification. In addition, trace amounts of partial oxidation products of glycerol were also observed by GC/MS, e.g., dihydroxyacetone, glyceraldehyde and glyceric acid. Under these conditions, as expected, silicalite was found to be inactive for glycerol oxidation.

In view of these results, a range of metallo-silicalites and MeAPO-5 catalysts were investigated for glycerol oxidation and the results are shown in table 1 for reaction at 20 and 70 °C. Only vanadium-containing catalysts (VS-1 and VAPO-5) were active at 20 °C. However, at all conversion levels investigated, even at 20 °C, the formate ester of glycerol and a complex range of acetals were the only products. At temperatures above 20 °C, vanadium-containing catalysts were too reactive with hydrogen peroxide and were not tested further. At 70 °C, TS-1, FeS-1 and CrAPO-5 were all active but, again, the same products were observed and only trace amounts of partial oxidation products were observed.

The MeAPO-5 catalysts were investigated further using conditions where the amount of hydrogen peroxide was restricted to give a maximum stoichiometric conversion level (based on one mole hydrogen peroxide per mole of glycerol, i.e., stoichiometric for partial oxidation) of 20, 50 and 100% (table 2). Again, the formate ester of glycerol and acetal were the dominant products even at low concentrations.

Since variation in reaction conditions (temperature, glycerol/hydrogen peroxide rates) or catalyst (silicalite containing Ti, Fe, V or AlPO-5 containing V, Cr, Co, Mn) did not lead to the formation of the partial oxidation products of glycerol, an alternative approach was adopted. It was decided to investigate the effect of pore diameter using Ti-containing catalysts (TS-1, Ti-MCM-41 and two commercial co-gel samples as described by McDaniel [14],

Table 1
Oxidation of glycerol with hydrogen peroxide.[a]

Catalyst	Temperature (°C)	Glycerol conversion (%)	Selectivity (%)		
			Formate ester	Hydroxyethanoic acid	Other[b]
None	20	0	–	–	–
	70	6.2	19	19	62
TS-1	20	0	–	–	–
	70	34.8	52	6	42
FeS-1	20	0	–	–	–
	70	31.9	55	3	42
VS-1	20	33.9	68	22	10
CrAPO-5	20	0	–	–	–
	70	36.9	61	11	28
VAPO-5A[c]	20	18.7	76	24	0
VAPO-5B[d]	20	25.3	65	29	6

[a] Reaction conditions: glycerol 10 g, H_2O_2 5 g (70% w/v), catalyst 0.25 g. Reaction time 24 h.

[b] Acetals plus traces of selective oxidation products.

[c] Reaction time 0.5 h.

[d] VAPO-5B contains half the amount of V compared with VAPO-5A.

Table 2
Oxidation of glycerol using decreased amounts of hydrogen peroxide.

Catalyst	Temperature (°C)	Theoretical conversion[a]	Conversion (%)	Product selectivity (%)		
				Formate ester	Hydroxyethanoic acid	Other
CrAPO-5	40	20	0	–	–	–
CrAPO-5	60	20	5.4	100	0	0
CrAPO-5	80	20	6.8	100	0	0
CrAPO-5	80	50[b]	9.6	81	0	19
CrAPO-5	80	100[c]	36.9	61	11	28
MnAPO-5	80	50[b]	11.6	68	0	32
CoAPO-5	80	50[b]	2.5	100	0	0

[a] Hydrogen peroxide amount adjusted to provide stoichiometric conversion level based on one mole hydrogen peroxide per mole glycerol. Reaction conditions: glycerol 5 g, hydrogen peroxide 1.23 g (30% w/v), 24 h.

[b] Hydrogen peroxide 3.1 g (30% w/v).

[c] Hydrogen peroxide 5 g (70% w/v).

Table 3
Oxidation of glycerol using Ti-containing materials.[a]

Catalyst	Pore size (nm)	Conversion (%)	Product selectivity (%)				
			Formate ester	Glyceraldehyde	Dihydroxyacetone	Glyceric acid	Other[b]
TS-1[c]	0.5	35	51	0	0	0	49
Ti-MCM-41	3.0	10	85	15	0	tr	tr
EP50od[c]	5.0	15	53	47	tr	tr	tr
EP50fd[c]	15.0	22	37	37	9	9	8

[a] Reaction conditions: glycerol 10 g, catalyst 0.25 g, H_2O_2 10 g (30% w/v), 80 °C, 24 h.

[b] Includes hydroxyethanoic acid.

[c] EP50 catalysts as described by McDaniel [14]: pore volume 2.35 ml g^{-1}, 550 $m^2\,g^{-1}$, 2.5 wt% Ti.

EP50 either oven dried (EP50od) or freeze dried (EP50fd) supplied by Unilever Research and Engineering). The results of glycerol oxidation under comparable conditions are given in table 3. It is apparent that wider pore catalysts do give partial oxidation, and now glyceraldehyde, dihydroxyacetone and glyceric acid are all observed. However, the conversion levels of glycerol achieved with these catalysts is quite low. This is to be expected due to the hydrophilic nature of the wider pore Ti-containing materials.

Leaching of transition metal ions is of particular concern when these types of materials are used for liquid-phase oxidation [14], especially vanadium- and chromium-containing systems, where it is known that transition metal ions in solution make a significant contribution to the observed catalysis. Since the catalyst pore size was found to have a significant influence on the product selectivity, it would be expected that transition metal ions in solution would be free of any pore restrictions, and thus should show excellent selectivity. However, this was not the case as the reaction conditions selected in this study (especially the presence of triol) did cause removal of the transition metals into solution, in particular V and Cr. In general, Ti-containing materials proved to be more stable under these conditions.

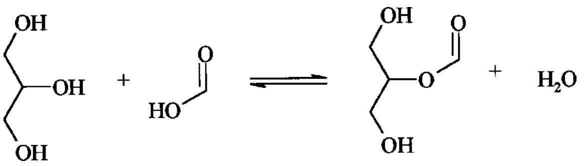
4. Discussion

4.1. Product formation

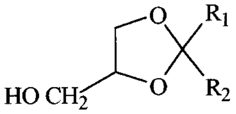
A range of metallosilicates (TS-1, FeS-1 and VS-1) with pore size ca. 0.5 nm and aluminophosphates with the AlPO-5 framework (pore size ca. 0.8 nm, containing V, Cr, Mn and Co) were all found to give similar products for the oxidation of glycerol and hydrogen peroxide. Whatever the conversion levels or reaction conditions, the major products were not the desired partial oxidation products but were formic acid and formate esters of glycerol. Previous studies have also observed C_1 and C_2 acids as by-products from glycerol oxidation [7,9]. Garcia et al. [7] reported the formation of oxalic acid and formic acid and the formic acid was subsequently oxidised to carbon dioxide. In addition, Fordham et al. [9] also reported the formation of trace amounts of formic acid for the oxidation of hydroxypyruvic acid. In the present study, hydroxyethanoic acid was also observed and it is possible that oxidative cleavage of the C_3 substrate could result in the formation of the C_2 hydroxyethanoic acid and formic acid. The formation of formic acid as the major product would require extensive oxidative cleavage and could involve a wide range of partial oxidation products, all of which would be readily sequentially oxidised.

It is apparent that the microporous catalyst, together with the reactive oxygen donor, hydrogen peroxide, provide ideal conditions for this complete oxidation. However, under the conditions used, formic acid does not decompose to carbon dioxide but reacts readily with glycerol to form an ester. In the studies of Garcia et al. [7] and Fordham et al. [9] Pd/C catalysts with dioxygen as oxygen donor were used and these systems preferentially give the partial oxidation products of glycerol.

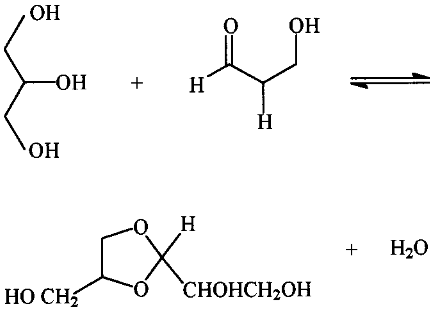
The ester is formed via a simple condensation reaction, for example,



It is clear that glycerol could form two monoesters, two diesters, plus a triester. In the present study, only the monoester was observed. This is due to the high concentration of water present under the reaction conditions utilised. In addition to the formate ester, acetals were also formed from glycerol with carbonyl compounds to give a series of 1,2-dioxolanes:



The major acetal observed was that formed from glycerol and glyceraldehyde ($R_1 = H$, $R_2 = CHOHCH_2OH$). This indicates that glyceraldehyde is formed in the reaction and is trapped in this way. Acetal formation is acid catalysed and, therefore, is catalysed by the formic acid formed in the reaction. However, the reaction forming an acetal is a condensation reaction:



The concentration of acetals formed is again dependent upon the concentration of water present. In the present study, due to the use of aqueous hydrogen peroxide, the formation of acetals is likely to be restricted. However, reaction conditions could be varied to restrict water levels, e.g., use of hydrogen peroxide extracted into organic solvents, and in such cases it is possible that acetals could become a preferred product. Other researchers have noted acetal formation in TS-1-catalysed oxidations [16,17]. Romano et al. [16] observed hemiacetal and acetal formation in the oxidation of 1-propanol. Huybrechts et al. [17] observed acetal formation in the oxidation of 1-octene in acetone as solvent. In this case, the octene epoxide product reacts via hydrogen to form the 1,2-diol which then reacted with acetone to form the corresponding acetal.

4.2. Effect of pore size

In the present studies, it was observed that the catalyst pore size was the most important parameter determining the selectivity of the products observed. As the pore size for Ti-containing catalysts increases from ca. 0.5 nm for TS-1 to 15 nm for the titania–silica co-gels, the selectivity to the formate ester is decreased and glyceraldehyde, dihydroxyacetone and glyceric acid are observed as products (figure 1). It is possible that, under the reaction conditions used in this study, the diffusion of products within the narrow pores leads to their facile over-oxidation, resulting in the formation of formic acid. As the pore size increases, so the diffusion limitations are decreased and the products of partial oxidation are observed. It is, therefore, clear that, for

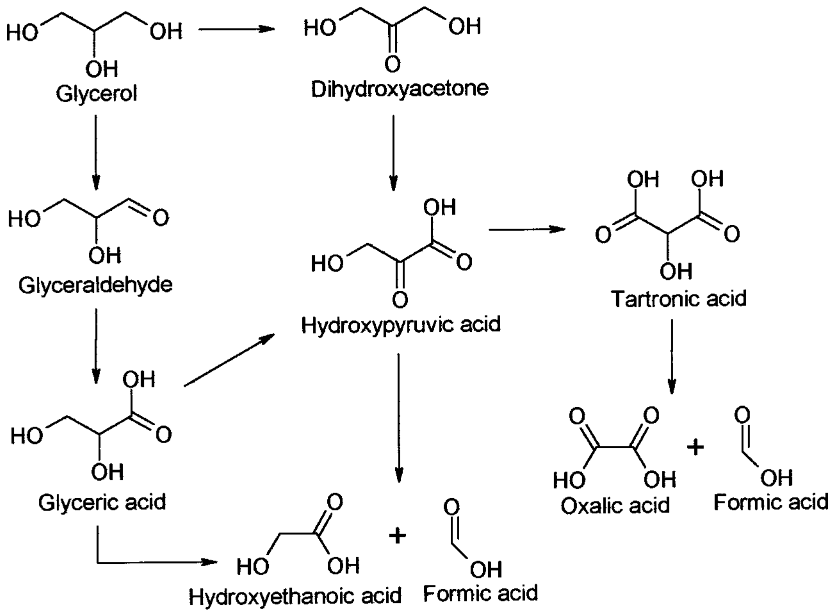


Figure 1. Possible reaction products for the partial oxidation of glycerol.

the oxidation of glycerol, it is important to use only macroporous catalysts to overcome any diffusion-related problems, which result in the products of non-selective oxidation.

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References

[1] M. Tarramasso, G. Perego and B. Notari, US Patent 4410501 (1983).

[2] A. Esposito, C. Neri and F. Buonomo, EU Patent 0102655 (1983).

[3] A.J.H.P. van der Pol and J.H.C. van Hoof, Appl. Catal. A 106 (1993) 97.

[4] F. Maspero and V. Romano, J. Catal. 146 (1994) 476.

[5] H. Hayashi, K. Kikawa, Y. Murai, N. Shigemoto, S. Sugiyama and K. Kawashioro, Catal. Lett. 36 (1996) 99.

[6] H. Kimura, K. Tsuto, T. Wakisaka, Y. Kazumi and Y. Inaya, Appl. Catal. A 96 (1993) 217.

[7] R. Garcia, M. Besson and P. Gallezot, Appl. Catal. A 127 (1995) 165.

[8] H. Kumura, Appl. Catal. A 105 (1993) 147.

[9] P. Fordham, R. Garcia, M. Besson and P. Gallezot, Stud. Surf. Sci. Catal. 101 (1996) 161.

[10] R. Szostak and T.L. Thomas, J. Catal. 100 (1986) 555.

[11] R. Szostak, V. Nair and T.L. Thomas, J. Chem. Soc. Faraday Trans. I 83 (1987) 487.

[12] S.T. Wilson and E.M. Flanigan, US Patent 4567029 (1986).

[13] B. Smith and O. Carlsson, Acta Chem. Scand. 17 (1963) 455.

[14] M.P. McDaniel, US Patent 4547557 (1985).

[15] R.A. Sheldon, M. Wallau, I.C.E. Arends and U. Schuchardt, Acc. Chem. Res. 31 485 (1998).

[16] V. Romano, A. Esposito, F. Maspero, C. Neri and M.G. Clerici, in: *New Developments in Selective Oxidation*, eds. G. Centi and F. Trifirò (Elsevier, Amsterdam, 1990).

[17] D.R.C. Huybrechts, I. Vaesen, H.X. Li and P.A. Jacobs, Catal. Lett. 8 (1991) 237.