Catal Lett (2012) 142:1114–1120
DOI 10.1007/s10562-012-0872-7

Oxidative Esterification of Homologous 1,3-Propanediols

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Received: 10 May 2012 / Accepted: 4 July 2012 / Published online: 19 July 2012

Abstract The oxidative esterification of a homologous series of diols (1,3-propanediol,2-methyl-propanediol and 2,2-dimethyl-1,3-propanediol) with methanol has been investigated using titania-supported gold, palladium and gold–palladium catalysts using molecular oxygen. The gold–palladium catalysts showed the highest activity and 1,3-propanediol was the most reactive while the additional methyl groups decreased the reactivity. However, it is possible to achieve high selectivity to methyl 3-hydroxypropionate and 2-methyl-3-hydroxyisobutyrate by mono-oxidations.

Keywords Gold catalysis · Gold palladium alloy nanoparticles · Oxidative esterification · Diol oxidation

1 Introduction

Methyl esterification is a ubiquitous methodology in organic synthesis [1]. Methyl esters are very useful chemical intermediates with respect to atom economy and versatility for further transformations [2]. Synthesis of esters from alcohols is traditionally a two-step procedure that includes conversion to carboxylic acids or activated carboxylic acid derivatives such as acid anhydrides or acid chlorides [3]. An alternative approach involves the carbonylation of aryl halides by transition-metal catalysts [4]. However, the high temperature and high CO pressures required, as well as the presence of halide anions, make this reaction environmentally unfavourable. Several relatively facile aldehyde esterifications with alcohols have been reported, in which stoichiometric amounts of oxygen donors are utilised, e.g. $KHSO_5$ or MnO_2 [5]. These methods require several reaction steps and produce unwanted by-products. Therefore, development of a catalytic, single-step, direct oxidative methyl esterification of alcohols under mild conditions is highly desirable from both economic and environmental points of view. Solid catalysts based on supported noble-metal nanoparticles have attracted tremendous recent attention owing to their unique catalytic properties for a broad spectrum of organic transformations, especially for the aerobic oxidation of alcohols. The formation of methyl esters by oxidising a primary alcohol over supported gold nano-particle catalysts in methanol has been reported [6–8]. The first examples of oxidative esterification of diols were reported by Kunugi [9, 10]. More recently, Hayashi et al. [6] showed that the selective oxidative esterification of ethylene glycol to methyl esters, by means of molecular oxygen, could occur using nano-gold particles supported on metal oxides as a slurry. Christensen and co-workers [11] have reported similar work with 1 % Au/TiO_2 as catalyst and reported 90 % selectivity to methyl 3-hydroxypropionate at 94 % conversion of 1,3-propanediol. Catalytic oxidation of 2-methyl-1,3-propanediol with $Pd\text{-}Bi/Al_2O_3$ in the presence of MeOH and air was reported by Tagawa et al. [12] to give 53 % methyl 3-hydroxyisobutyrate. The oxidation of 2,2-dimethyl-1,3-propanediol has, to date, received little attention, Hong et al. [13] showed that using Pd/C as catalyst in air led to the formation of 3-hydroxy-2,2-dimethylpropionic acid, while a gas-phase oxidation of this diol over alkali-exchanged zeolites gives 2-methylpropanal, 2-methylbutanal and traces of 3,3-dimethyloxetane [14].

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We have previously investigated the oxidative esterification of 1,2-propanediol to form methyl lactate and methyl pyruvate [15] using supported Au, Pd and AuPd nanoparticles. In this paper we have now extended this study, we have investigated if homologous C_3-based propanediols are able to undergo selective oxidation to their corresponding methyl hydroxy-esters by carrying out a noble-metal catalysed aerobic oxidation in methanol. The substrates investigated were 1,3-propanediol,2-methyl-1,3-propanediol and 2,2-dimethyl-1,3-propanediol. The choice of these substrates was made in order to have polyols with hydroxyl groups in primary positions with additional methyl groups. In this paper we report the findings of this investigation.

2 Experimental

2.1 Preparation of the Catalysts by the Sol-Immobilisation Method

An aqueous solution of $PdCl_2$ (Johnson Matthey) and $HAuCl_4 \cdot 3H_2O$ of the desired concentration was prepared. Polyvinylalcohol (PVA) (1 wt% solution, Aldrich, MW = 10,000, 80 % hydrolyzed) was added (PVA/Metal (by wt) = 1.2); 0.1 M freshly prepared solution of $NaBH_4$ (>96 %, Aldrich, $NaBH_4$/Au (mol/mol) = 5) was then added to form a dark-brown sol. After 30 min of sol generation, the colloid was immobilized by adding titania oxide (Degussa P25, SA = 49 m^2/g, 80 % anatase), acidified to pH 1 with sulfuric acid, under vigorous stirring. The amount of support material required was calculated so as to have a total final metal loading of 1 wt%. After 2 h the slurry was filtered, the catalyst washed thoroughly with distilled water (neutral mother liquors) and dried at 120 °C overnight. The catalyst was prepared using a 1:1 molar ratio of Au:Pd (denoted as 1 %AuPd(1:1)/TiO_2). Monometallic catalysts containing gold or palladium (for the Pd monometallic catalysts a small amount of aqueous HCl was added to aid dissolution of $PdCl_2$) were also prepared using similar methodology, and these are denoted 1 %Au/TiO_2 and 1 %Pd/TiO_2. Analysis confirmed the metal concentration was as specified, and we have used these catalysts for redox reactions previously and have found them to be reusable without significant loss of activity or metal content.

2.2 Catalyst Characterisation

The catalysts were characterised using X-ray photoelectron spectroscopy (XPS). Spectra were recorded on a Kratos Axis Ultra DLD spectrometer employing a monochromatic AlKα X-ray source (120 W) and analyser pass energies of 160 eV (for survey scans) or 40 eV (for detailed scans). Samples were mounted using double-sided adhesive tape and binding energies referenced to the C(1 s) binding energy of adventitious carbon contamination which was taken to be 284.7 eV.

2.3 Oxidative Esterification Reactions

Oxidative esterification reactions were carried out using a 50 ml Radleys low pressure reactor with a maximum working pressure of 4 bar. The reactor was charged with 1,3-propanediol,2-methyl-1,3-propanediol or 2,2-dimethyl-1,3-propanediol (1.5 mmol), sodium hydroxide (1.5 mmol, 0.06 g), methanol (7.9 g) and catalyst (substrate/metal molar ratio = 500/1). The reaction vessel was sealed, purged 3 times with oxygen and pressurized to 3 bar with O_2; the oxygen inlet remained open throughout the reaction so that oxygen was replenished as it was consumed. The reaction mixture was stirred (1,000 rpm) and heated to 80 °C. Reactions were cooled to 20 °C periodically and samples were taken. The reactor was then recharged with oxygen and reheated to 80 °C. The isolated reaction mixtures were concentrated under vacuum and analysed by ^{1}H and ^{13}C NMR spectroscopy. Conversions and selectivities were calculated from NMR spectra via integration of the starting material and the products. These analyses were confirmed by additional GC analysis which was carried out using a Varian 3,800 chromatograph equipped with a CP 8,400 autosampler and CP-wax 52 column. Products were identified by comparison with authentic samples, and quantification, and hence yields, were established using an external standard.

2.4 Results and Discussion

The three catalysts used in this study 1 %Au/TiO_2, 1 %Pd/TiO_2 and 1 %AuPd(1:1)/TiO_2 have been extensively characterised previously using scanning transmission electron microscopy [16–19]. The metal particle size for the catalysts prepared by sol-immobilisation was observed to be between 4 and 7 nm [16, 17]. The AuPd nanoparticles were all found to comprise homogeneous alloys and no core–shell structures were observed. As the catalysts had been well characterised previously we have used them in the present study. However, we have carried out some additional XPS characterisation (Table 1) to complement the detailed microscopy studies [16–19]. The XPS data showed that the catalysts contain predominantly metallic Au^0, and Pd^0 species as indicated by binding energies of 83.1 and 334.9 eV for the respective metals; the low binding energy of the Au($4f_{7/2}$) signal attributable to small (typically <5 nm) particles as observed by Radnik et al. [20] for Au on TiO_2 prepared by several methods. The

Table 1 XPS-derived surface elemental compositions for the catalysts prepared by sol-immobilisation

Catalyst	Au (at%)		Pd (at%)		Oxidation state
	Fresh	Used	Fresh	Used	
1 %Pd/TiO_2	–	–	0.30	0.12	$Pd^0 + Pd^{2+}$
1 %Au/TiO_2	0.26	0.18	–	–	Au^0
1 %AuPd/TiO_2	0.29	0.31	0.12	0.80	Au^0, Pd^0

Data are shown for the unused catalysts and also after use for 1,3-propanediol oxidation

monometallic Pd/TiO_2 catalyst does exhibit some Pd(II) as evidenced by a shoulder to higher binding energy (336.7 eV); however, after reaction there is no discernible amount of Pd(II). For the monometallic catalysts the decrease in metal content in the external layer of the catalyst after the reaction could reflect sintering of the metal particles. The redistribution of the elements on the surface would also lead to similar phenomenon. However, the Au–Pd/TiO_2 sample reveals an increase in the amount of Pd, whilst the Au remains constant (within experimental accuracy) and may be attributed to highly re-dispersed Pd sites. The observed molar ratio of metals for the bimetallic catalysts is consistent with the absence of core–shell structures.

Oxidative esterification of 1,3-propanediol was carried out over 1 %Au/TiO_2, 1 %Pd/TiO_2 and 1 %AuPd(1:1)/TiO_2. The main product observed was methyl 3-hydroxypropionate with notable amounts of the sodium salt of 3-hydroxypropionic acid. It appears that methyl 3-hydroxypropionate is stable under these conditions and not oxidised further to other products (only traces of dimethyl malonate were detected). The 3-hydroxypropionic acid may arise from the hydrolysis of methyl 3-hydroxypropanoate formed during the reaction (Scheme 1). Formation of the corresponding ether, methyl 3-methoxypropanoate, was unexpected but its formation can easily be rationalized by a base-catalysed E_1cB elimination of water from methyl 3-hydroxypropanoate to give methyl acrylate which would be expected to undergo very rapid Michael addition of methanol under such conditions (Scheme 1). Direct Williamson-type *O*-alkylation seem much less likely given the reagents present. Formic acid and methyl formate are also observed and these originate from oxidation of methanol that proceeds in parallel with the oxidative esterification. Low amounts of carbon oxides, particularly CO_2, are observed as the products of the over-oxidation of the diol or methanol.

The monometallic Pd catalyst supported on titania was more active than the Au catalysts (Table 2). However, the monometallic Pd catalysts only gave ca. 80 % carbon mass balance for the identified products. This was because the monometallic Pd catalysts gave CO_2 as a product but this could not be collected and accurately quantified in this reactor set up. Previous studies of alcohol oxidation with monometallic Pd catalysts have also shown this to be the case [21]. By comparison, the bimetallic 1 %Au–Pd/TiO_2 catalyst was moderately active and retained high selectivity

Scheme 1 A proposed reaction scheme of oxidation of 1,3-propanediol in methanol in presence of *base* over noble-metal catalysts. Observed products are highlighted in *boxes*

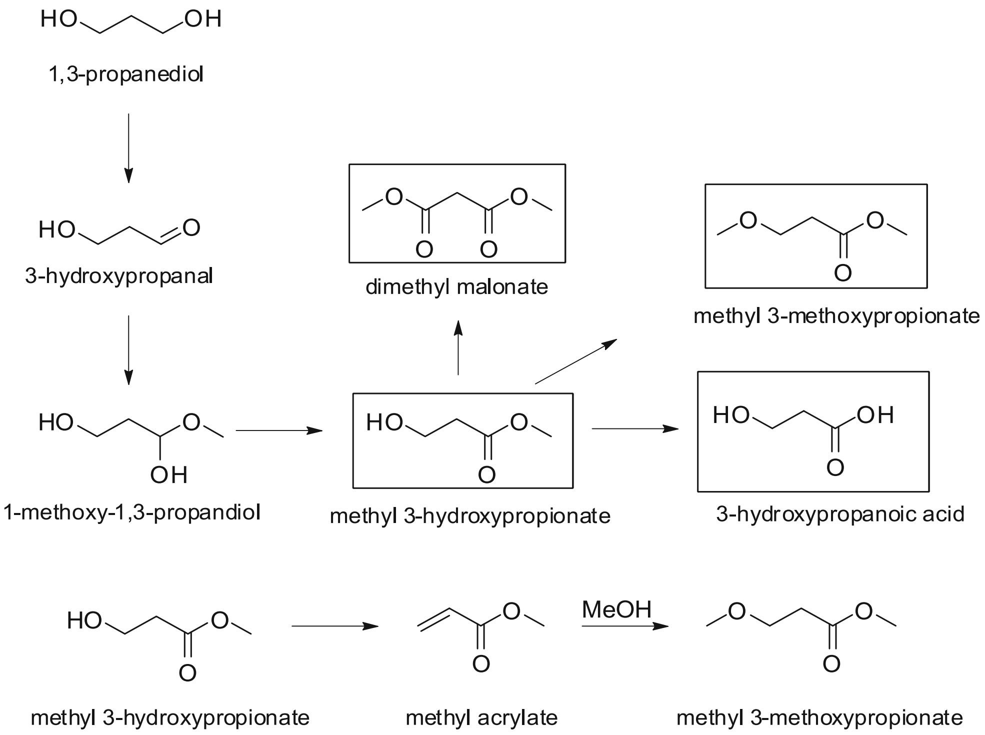


Table 2 1,3-propanediol oxidative esterification

Catalyst	Time (h)	Conversion (%)	3MHP selectivity (%)	3HPA selectivity (%)
1 %Au/TiO$_2$	2	10	87	12
	4	18	84	15
	24	39	82	17
1 %Pd/TiO$_2$	2	41	95	5
	4	61	88	12
	24	69	82	7
1 %AuPd (1:1)/TiO$_2$	2	20	88	11
	4	28	82	18
	24	45	80	19

3MHP methyl 3-hydroxypropionate, *3HPA* 3-hydroxypropanoic acid (sodium salt)

Table 3 Oxidation of 2-methyl-1,3-propanediol

Catalyst	Time (h)	Conversion (%)	MHB selectivity (%)	HBA selectivity (%)
1 %Au/TiO$_2$	2	10	60	39
	4	12	75	14
	24	46	93	7
1 %Pd/TiO$_2$	2	21	99	–
	4	30	72	28
	24	62	55	45
1 %AuPd (1:1)/TiO$_2$	2	16	90	10
	4	22	91	9
	24	37	79	20

MHB methyl hydroxyisobutyrate, *HBA* hydroxyisobutyric acid

Table 4 Oxidation of 2,2-dimethyl-1,3-propanediol

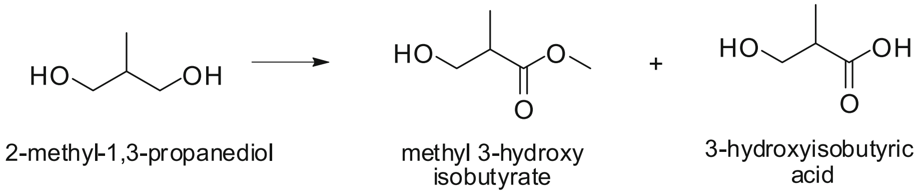
Catalyst	Time (h)	Conversion (%)	MHP selectivity (%)	HPA selectivity (%)	HPAld selectivity (%)
1 %Au/TiO$_2$	2	7	60	40	–
	4	10	60	40	–
	24	30	73	26	–
1 %Pd/TiO$_2$	2	11	15	15	69
	4	12	21	17	62
	23	15	22	16	61
1 %AuPd (1:1)/TiO$_2$	2	18	61	11	26
	4	22	62	28	10
	23	25	60	32	7

MHP methyl 3-hydroxypivalate, *HPA* 3-hydroxypivalic acid, *HPAld* 3-hydroxypivalic aldehyde

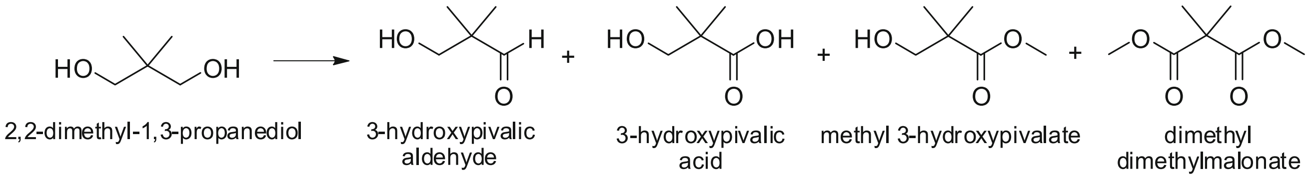
to the major product (80 % selectivity at 45 % conversion after 24 h) and in this case the mass balance was closed. Nevertheless, the performance of the 1 %Pd/TiO$_2$ catalyst showed that it is active after 2 h giving 90 % selectivity to the major product at 41 % conversion, which is competitive with the results achieved in previous studies [6, 11].

Oxidations of 2-methyl-1,3-propanediol and 2,2-dimethyl-1,3-propanediol were carried out under the same conditions as the experiments with 1,3-propanediol. The oxidation results showed hydroxy-ester and hydroxy-acid to be the major reaction products (Tables 3, 4). Interestingly, the oxidation is taking place at only one alcohol functionality in all of the three substrates studied. This chemoselectivity may indicate that the second alcohol group is influenced by the presence of a methyl ester group making it more difficult to oxidise (Scheme 2). Oxidative esterification of 2-methyl-1,3-propanediol leads to the formation of methyl 3-hydroxyisobutyrate in high selectivities (Table 3; Scheme 2). Reactions over 1 %Pd/TiO$_2$ resulted in a selectivity of 99 at 21 % conversion after 2 h; however, the selectivity decreased at longer reaction times. Conversely reactions over 1 %Au/TiO$_2$ retained selectivity to the major product at higher conversion (93 % selectivity to methyl hydroxyisobutyrate at 46 % conversion after 24 h). This shows the influence that Au has on modifying the catalytic performance of Pd by maintaining the selectivity to the desired ester product. From this point of view, this process can be considered as a potential route from 2-methyl-propanediol through methyl 3-hydroxyisobutyrate to a large scale chemical such as methyl methacrylate [22]. These results are essentially the same as those obtained from oxidations of the parent 1,3-propanediol (Table 2).

The peculiarity of 2,2-dimethyl-1,3-propanediol oxidation was that the hydroxy-aldehyde was obtained as the reaction product (Scheme 3), in the reactions catalysed by palladium (Table 4). When oxidizing 1,3-propanediol and 2-methyl-1,3-propanediol in methanol, we observed no aldehyde formation, suggesting that it is an intermediate that is rapidly oxidised either into the corresponding hydroxy-acid or hydroxy-ester. The reactivity of 2,2-dimethy-1,3-propanediol is higher over 1 %Au–Pd(1:1)/TiO$_2$, although oxidation does not continue to completion



Scheme 2 A proposed reaction scheme of oxidation of 2-methyl-1,3-propanediol in methanol in presence of *base* over noble-metal catalysts



Scheme 3 A proposed reaction scheme of oxidation of 2,2-dimethyl-1,3-propanediol in methanol in presence of *base* over noble-metal catalysts

and hence we observe a decrease in the rate of reaction with this system over longer reaction times. By comparison, prolonged reactions with 1 %Au/TiO$_2$ indicated that activity is retained (Fig. 1), and appears to maintain selectivity to the major product.

Methyl substituted homologous propanediols are oxidised more slowly than 1,3-propanediol. With respect to the general trend of reactivity of the different propanediols substrates to oxidation, the rate of oxidation decreases with the addition of methyl groups, following the order: 1,3-propanediol > 2-methyl-1,3-propanediol > 2,2-dimethyl-1,3-propanediol. Only in the case of 1 %Au/TiO$_2$ is the initial reactivity of all three substrates found to be similar (Figs. 2, 3, 4).

The difference in reactivity between 1,3-propanediol and its homologs is likely due to the different steric hindrance around the OH group in the different alcohols. In particular molecular modeling using B3LYP/6-31G(d,p) (All calculations carried out using the Gaussian09 package [23]) of the first dehydrogenation product, 3-hydroxypropanal and its methylated analogues, show that the lowest energy structures have the aldehyde group away

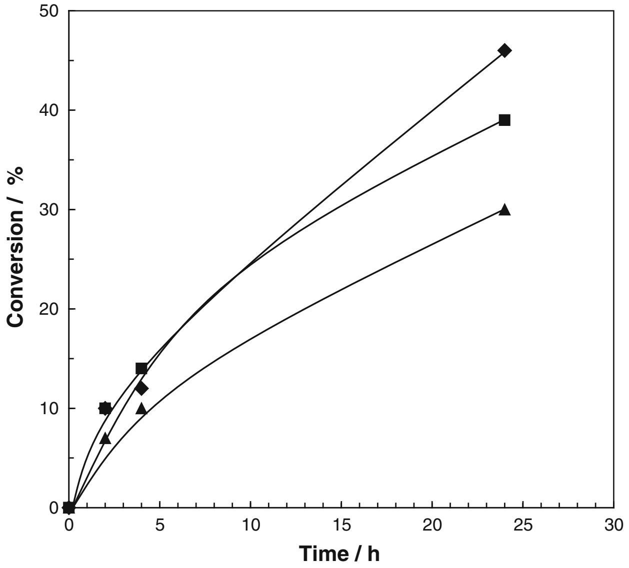


Fig. 2 Oxidation of homologous propanediols using 1 %Au/TiO$_2$. Conversion of 1,3-propanediol (*filled square*), conversion of 2-methyl-1,3-propanediol (*filled diamond*), conversion of 2,2-dimethyl-1,3-propanediol (*filled triangle*)

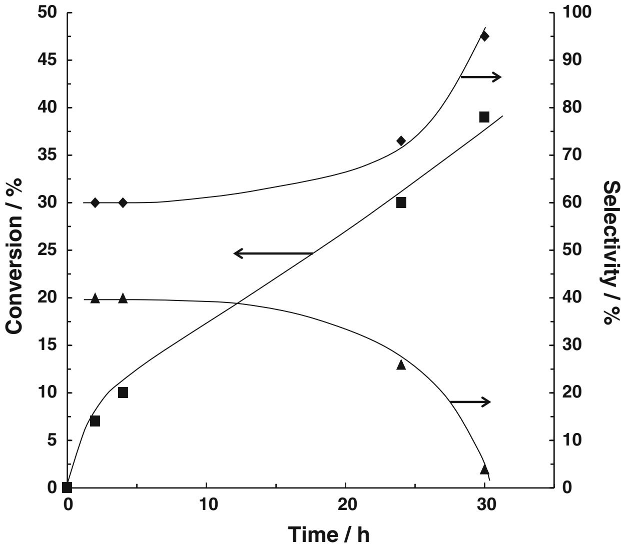


Fig. 1 Effect of time on the oxidative esterification of 2,2-dimethyl-1,3-propanediol over 1 %Au/TiO$_2$. Conversion of 2,2-dimethyl-1,3-propanediol (*filled square*), selectivity to methyl 3-hydroxypivalate (*filled diamond*), selectivity to 3-hydroxypivalic acid (*filled triangle*)

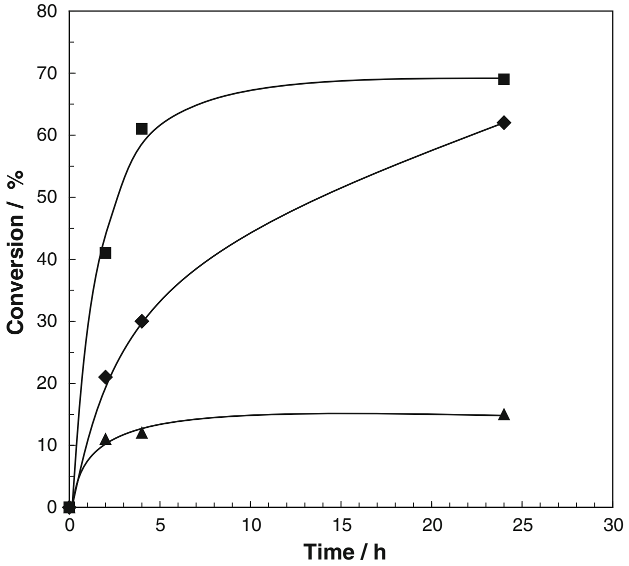


Fig. 3 Effect of time on the oxidation of homologous propanediols over 1 %Pd/TiO$_2$. Conversion of 1,3-propanediol (*filled square*), conversion of 2-methyl-1,3-propanediol (*filled diamond*), conversion of 2,2-dimethyl-1,3-propanediol (*filled triangle*)

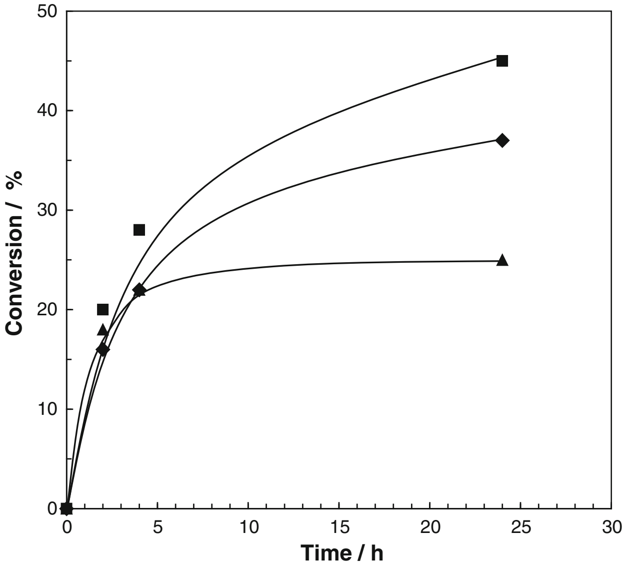


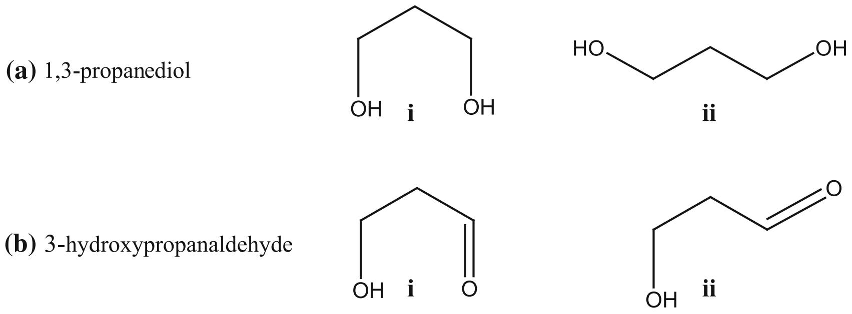
Fig. 4 Oxidation of homologous propanediols using 1 %AuPd(1:1)/TiO_2. Conversion of 1,3-propanediol (*filled square*), conversion of 2-methyl-1,3-propanediol (*filled diamond*), conversion of 2,2-dimethyl-1,3-propanediol (*filled triangle*)

Table 5 Calculated (B3LYP/6-31G(d,p)) [23] relative energies for conformations of 1,3-propanediol oxidative esterification

Molecule	Conformer [a]	Relative energy/kJ/mol
1,3-Propanediol	i	0
	ii	16
2-Methyl-1,3-propanediol	i	0
	ii	19
2,2-Dimethyl-1,3-propanediol	i	0
	ii	19
3-Hydroxypropanaldehyde	i	0
	ii	19
2-Methyl-3-hydroxypropanaldehyde	i	0
	ii	14
2,2-Dimethyl-3-hydroxypropanaldehyde	i	0
	ii	16

Note [a] Conformers defined as in Fig. 5

from substituents at the 2-position (Table 5). This conformation is stabilized by an internal hydrogen bond. For the substrates with a methyl group in the 2-position this results in steric crowding of the aldehyde C atom (Fig. 5). This centre has to be approached by methanol to form the hemiacetal (1-methoxy-1,3-propanediol) shown in Scheme 1 and so this step in the reaction will be slower for methylated substrates. We suggest that since the double bond of the aldehyde group will interact more strongly with the metal component of the catalyst than it will with the alcohol of the substrate; site blocking by this intermediate



(c) 2,2-dimethyl-3- hydroxypropanaldehyde

d) 2,2-dimethyl- 3-hydroxypropanaldehyde

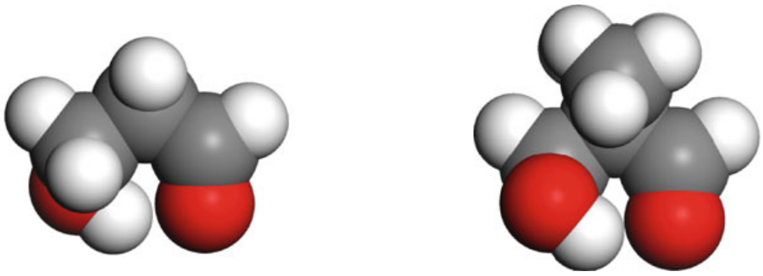


Fig. 5 **a** and **b** Chemical structure representations of the **i** and **ii** conformations for the examples of 1,3-propanediol and hydroxypropanaldehyde, in each case an internal hydrogen bond stabilises the **i** conformation, **c** and **d** optimised structures for 2,2-dimethylhydroxypropanaldehyde and 2,2-dimethyl- hydroxypropanaldehyde in the **i** conformation. CPK spheres are set at 0.7 of the van der Waals radius for each atom. Atom colours, C : *grey*, O : *red* and H : *white*

will occur. This will be particularly true for catalysts containing Pd, since the aldehyde interaction with Au particles will be considerably weaker than with Pd. A more detailed study is still underway, at present we suggest that the substrate reactivity is also affected by diffusion of reactants within the catalyst and the strength of surface interaction of reactants with the catalyst surface. Both of these effects will be less important for 1,3-propanediol where the OH groups are more accessible than for 2-methyl-1,3-propanediol or 2,2-dimethyl-1,3-propanediol, which is consistent with the catalytic data observed.

Although a more detailed study of the reaction mechanisms is required, at present, we propose that the reaction path is likely to be as shown in Scheme 1. The final products, hydroxy-esters and hydroxy-acids, were detected in all reactions due to oxidation of all three of the examined substrates. Methyl-3-methoxypropionate was also observed as a product of 1,3-propanediol oxidative esterification which we consider arises via a sequential elimination-Michael addition sequence in the presence of base. A hydroxy-aldehyde was detected only as a product of 2,2-dimethyl-1,3-propanediol oxidation, whereas the hemi-acetal was identified as the key intermediate of ester formation previously [24]. This could be associated with the lack of an α-H but, more likely, is a consequence of the much greater steric crowding in this substrate and its products.

3 Conclusions

The oxidation of 1,3-propanediol,2-methyl-propanediol and 2,2-dimethyl-1,3-propanediol over supported noble-metal catalysts in methanol was investigated. Using supported gold palladium catalysts it was possible to tune the catalytic reactivity and selectivity to the desired products for the oxidative esterification of 1,3-propanediols to hydroxy-esters in the liquid-phase using molecular oxygen. Introducing the methyl substituents into the propanediol substrate decreased the reactivity of the substrate to oxidation. It was possible to achieve high selectivity to methyl 3-hydroxy-propionate and 2-methyl-3-hydroxyisobutyrate which potentially could be applied to the production of chemicals such as methyl acrylate and methyl methacrylate on a large scale.

Acknowledgments This work formed part of the Glycerol Challenge and Tennants Fine Chemicals Ltd and the Technology Strategy Board are thanked for their financial support. This project is co-funded by the Technology Strategy Boards Collaborative Research and Development programme, following an open competition. The Technology Strategy Board is an executive body established by the Government to drive innovation. It promotes and invests in research, development and the exploitation of science, technology and new ideas for the benefit of business—increasing sustainable economic growth in the UK and improving quality of life. For more information visit www.innovateuk.org.

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