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The selective oxidation of 1,2-propanediol to lactic acid using mild conditions and gold-based nanoparticulate catalysts

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ABSTRACT

The use of bio-renewable resources for the generation of materials and chemicals continues to attract significant research attention. It is well established that glycerol is an excellent starting material for the production of 1,2-propanediol by dehydration/hydrogenation and that this can subsequently be oxidised to lactic acid, which has the potential to be used as a major chemical in the production of biodegradable polymers. Previous studies using gold catalysts for the oxidation of 1,2-propanediol have used elevated temperatures and pressures. We now show that the oxidation of 1,2-propanediol to form lactic acid can be carried out selectively under mild reaction conditions with gold–platinum catalysts prepared using a sol-immobilisation method, with activated carbon as the support. Carrying out the reaction at ambient temperature with air significantly improves the reaction in terms of its environmental impact and its industrial attractiveness, as lactic acid can be obtained with high selectivity.

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1. Introduction

Lactic acid has the potential to be a major intermediate in the production of biodegradable polymers. Currently, lactic acid is used mainly as a fine chemical, with applications in the cosmetic, textile and food industries. The realisation that polylactate is a biodegradable plastic [1] has led to an enhanced interest in the transformation of 1,2-propanediol into lactic acid, which could ultimately result in the latter becoming a commodity rather than a fine chemical.

A synthetic process for producing lactic acid has been reported by Prati and Rossi [2], which involves the reaction of acetaldehyde and HCN along with a subsequent treatment with sulphuric acid. However, this reaction is considered not to be very 'green' in character due to the nature of the chemicals used and the waste products generated. Lactic acid is mainly produced by a fermentation process [1], which requires high dilutions and has a slow rate of reaction as the enzyme action is inhibited by the reaction product. Therefore, there is a definite need to produce lactic acid *via* a greener route which this paper addresses by describing the oxidation of 1,2-propanediol to form lactic acid under mild, catalytic conditions.

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Glycerol is currently a desirable starting material for the production of value-added fine chemicals, being a bio-renewable feedstock that is a by-product of the manufacture of bio-diesel [3]; and with the current drive towards developing greener fuel sources, the availability of glycerol as a raw material is likely to be sustained. Glycerol has been shown to be an excellent starting material for the production of 1,2-propanediol by dehydration/hydrogenation, as has been reported by Miyazawa et al. [4]. Furthermore, 1,2propanediol has been shown to be an effective intermediate for the production of lactic acid. Initial work by Tsujino et al. [5] using Pd/C catalysts modified with Pb, Bi and/or Te, using aqueous conditions at pH 8 and 90°C, to oxidise at both the primary and secondary alcohol groups, led not only to the formation of lactic acid, but also to hydroxyacetone and pyruvic acid. Pinxt et al. [6] showed that pyruvic acid was produced via two parallel pathways from either lactic acid or hydroxyacetone using Pt modified by Pb, Bi and Sn supported on carbon. These studies indicated that 1,2propanediol can effectively be converted to lactic acid, but the use of Pd and Pt catalysts to do so leads to low selectivity for the desired product.

Recently, interest has grown in using highly stable gold nanoparticles for oxidation reactions [7]. Nano-particulate gold dispersed on a range of oxide supports and carbon has been studied for a wide range of catalytic redox reactions, such as CO oxidation [8,9] and CO oxidation in the presence of H₂, H₂O and CO₂ for fuel cell

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applications [10,11]. Gold nanoparticles have also been shown to be effective for the oxidation of alkenes [12] and alcohols [13], including polyols such as glycerol [14,2,15]. Rossi and Prati were the first to show that supported gold nanoparticles were effective for alcohol oxidation in the presence of base [16,17]. A number of more recent studies have concentrated on the role of the gold particle size [18], the catalyst pre-treatment [19] and catalyst preparation method [20] on alcohol oxidation. Prati and Rossi were also the first to demonstrate that gold supported on carbon could be used to oxidise 1,2-propanediol to form lactic acid [21], with high conversion and selectivity at O₂ pressure of 3 bar and temperature of 90 °C.

We have demonstrated that alloying gold with palladium leads to a significant enhancement of activity, with a simultaneous retention of selectivity for alcohol oxidation to the corresponding aldehyde [22]. Such catalysts also markedly improve the yield of hydrogen peroxide in its direct synthesis from hydrogen and oxygen [23-28]. In these earlier studies we used a wet impregnation preparation method to generate the gold-palladium nanoparticles. Recently, we have shown that a sol-immobilisation method can give mono-metallic Au and Pd, and bi-metallic Au-Pd supported nanoparticles with enhanced activity for glycerol oxidation [29]. We have also demonstrated that wet impregnation and solimmobilisation prepared Au–Pd catalysts, supported on TiO₂, and C are effective for the formation of lactic acid from 1,2-propanediol. Sol-immobilisation catalysts proved to be the most effective, giving 96% selectivity at 94% conversion at 60 °C and 10 bar O₂ [30]. In this present paper, we extend our earlier studies of 1,2-propanediol oxidation with Au-Pd materials to Au-Pt catalysts, and we now show that by tailoring the catalyst composition together with the reaction conditions, choice of support and reactor type, significant activity for the oxidation of 1,2-propanediol can be achieved under much milder conditions than those previously reported. The decrease in reaction temperature and the use of air as an oxidant means the catalytic oxidation is more environmentally friendly and the simplified nature of the reaction makes it more appealing as an industrial process. Furthermore, the drive towards milder conditions could help prevent alternative oxidation pathways, reducing the formation of the undesired product, pyruvic acid.

2. Experimental

2.1. Catalyst preparation

A series of Au, Pt, Pd, Au–Pd, Au–Pt and Pd–Pt catalysts supported on activated carbon (KB-B, G60, KB, Aldrich; Table 1 compares the textural properties of these three supports) were prepared using a sol-immobilisation method. Aqueous solutions of PdCl₂ (Johnson Matthey) or H₂PtCl₆ (Johnson Matthey) and HAuCl₄·3H₂O (Johnson Matthey) of the desired concentration were prepared. To this solution polyvinylalcohol (PVA) (1 wt% solution, Aldrich, weight average molecular weight $M_W = 9000-10,000 \text{ g mol}^{-1}$, 80% hydrolysed) was added (PVA/Au (wt/wt) = 1.2). Subsequently, a freshly prepared 0.1 M solution of NaBH₄ (>96%, Aldrich, NaBH₄/metal (mol/mol) = 5) was added to form a sol. After 30 min of sol generation, the colloid was immobilised by adding activated carbon (acidified to pH 1 by sulphuric

Table 1

Structural properties of the carbon supports used in this study.

Activated carbon support	Surface area (m ² /g)	Pore volume (ml/g)
G-60	600	0.95
KB	1500	2
KB-B	1500	2

acid) under vigorous stirring. The amount of support material required was calculated to give a total final metal loading of 1 wt%. After 1 h the slurry was filtered, the catalyst washed thoroughly with distilled water and dried at 110° C overnight.

2.2. Catalyst testing

Reactions were carried out using a 50 ml Radleys low pressure reactor. NaOH (0.48 g or 0.96 g) was dissolved in 1,2-propanediol (20 ml, 0.6 M aqueous solution). The catalyst was added to the solution (molar ratio substrate:metal = 1000–16,000) in a round bottom flask. The flask was charged with oxygen to the desired pressure (1–3 bar), and heated to the required temperature (30–60 °C), whereupon stirring was started. The solution temperature was maintained for the desired reaction time (30–240 min), then cooled to room temperature and the reaction mixtures were analysed by HPLC and NMR spectroscopy.

The reaction was also performed on a larger scale in a 500 ml wide neck flask with a water cooled jacket and a three neck flat flange lid. The flask contained four plastic inserts to aid the formation of vortices within the reaction mixture. A thermometer was inserted into the central neck of the flange lid to monitor the reaction temperature. The second neck was connected to a condenser and the third neck had a rubber stopper through which (i) air was bubbled into the reaction mixture at atmospheric pressure and (ii) reaction samples were obtained. The 0.5%Au + 0.5%Pt/C catalyst (substrate:metal mol ratio = 5000 molar ratio) was added to the solution at 25 °C and samples were obtained at various time intervals (30–120 min). The samples were passed through a 0.22 μ m syringe filter to remove the catalyst, and then activated charcoal, and finally the filtered reaction mixture was analysed by HPLC.

HPLC analysis was carried out using a Varian 920-LC fitted with a metacarb 87H column with ultraviolet and refractive index detectors. Reactants and products were separated using a metacarb 67H column. The eluent was a solution of H_3PO_4 (0.01 M) with a flow of 0.3 ml min⁻¹. Samples of the reaction mixture (0.5 ml) were diluted to 5 ml using the eluent. Products were identified by comparison with known pure samples. For quantification of the starting material and products an external calibration method was used and the calibration factor for each was calculated.

¹H NMR spectroscopy was used for product identification: spectra were acquired over a 16 scan period on a Bruker 400 MHz DPX system using a 5 mm auto tune broadband probe. All samples were prepared with D₂O.

2.3. Catalyst characterisation

X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Ultra DLD spectrometer employing a monochromatic AlK_{α} 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(1s) binding energy of adventitious carbon contamination which was taken to be 284.7 eV.

Samples for examination by scanning transmission electron microscopy (STEM) were prepared by dispersing the dry catalyst powder onto a holey carbon film supported by a 300 mesh copper TEM grid. STEM high angle annular dark field (HAADF) images of the bimetallic particles were obtained using an aberration corrected JEOL 2200FS (S)TEM operating at 200 kV. X-ray energy dispersive (XEDS) spectra were acquired from individual nanoparticles larger than 1–2 nm in size while rastering the beam over the entire particle.

Table 2

Effect of the activated carbon support identity when using Au–Pt supported nanoparticles for the selective oxidation of 1,2-propanediol.^a

Support	Conversion (%)	Selectivity (%)				
		Lactate	Formate	Acetate		
G60	70	86	4	10		
KB	76	89	3	8		
KB-B	80	89	2	9		

^a Reaction conditions: catalyst AuPt = 1:1; 1 wt% total metal; water (20 ml); 1,2propanediol (0.6 mol); NaOH/1,2-propanediol molar ratio = 1; reaction temperature, $40 \degree C$; substrate:metal mol ratio = 2000; reaction time = 4 h; TOF calculated at 4 h on the basis of total metal loading; stirrer speed = 1000 rpm.

3. Results and discussion

3.1. Effect of the activated carbon support

Three Au–Pt catalysts were prepared using the same starting colloidal sol and the three activated carbon supports. These were then evaluated as catalysts for the oxidation of 1,2-propane diol and the results (Table 2) show that the catalysts all gave relatively high conversions for this reaction. The catalyst prepared using the KB-B activated carbon gave a slightly enhanced conversion as compared to the others under identical reaction conditions. Hence, the highest catalytic activity was obtained with a support possessing a high

Table 3 Effect of supported nanoparticles identity on the selective oxidation of 1,2 propane diol.^a

	-	-								
Catalyst	NaOH/S ^b	Conversion (%)	Selectivity (Selectivity (%)						
			Lactate	Formate	Acetate	Hydroxy acetone	Pyruvate	TOF (h ⁻¹)		
	2	46	67	4	29	0	0	460		
Au	1	30	62	3	35	0	0	300		
Pd	2 or 1	<1	-	-	-	_	-	-		
Pt	2 or 1	<1	-	-	-	_	-	-		
	2	50	92	2	6	0	0	500		
Au-Pt	1	78	86	3	11	0	0	780		
	2	61	87	1	12	0	0	610		
Au-Pd	1	52	81	2	17	0	0	520		
D 1 D	2	33	94	1	4	0	0	330		
Pd-Pt	1	22	96	4	0	0	0	220		

^a *Reaction conditions*: water (20 ml); 0.6 M 1,2-propanediol; 1,2-propanediol/total metal ratio = 4000; O₂ 3 bar at 40 °C; reaction time 4 h; TOF calculated at 4 h on the basis of total metal loading; stirrer speed = 1000 rpm; support used activated carbon KB-B.

^o NaOH:substrate molar ratio.

Table 4

Effect of Au-Pt bimetallic catalyst loading on the selective oxidation of 1,2-propanediol at 60 °C.ª

Catalyst	NaOH/S ^b	Selectivity (%)					
		Conversion (%)	Lactate	Formate	Acetate	$TOF(h^{-1})$	
10/D+	2	6	96	0	4	30	
1%Pt	1	3	97	0	3	15	
0.05% 0.05% 0.05%	2	69	95	0	5	345	
0.95%Pt + 0.05%Au	1	70	93	1	6	350	
0.0% Dt + 0.1% A	2	88	96	0	4	440	
0.9%Pt+0.1%Au	1	85	93	2	5	425	
0.75% 0.0.25% 4	2	95	96	0	4	475	
0.75%Pt+0.25%Au	1	90	93	1	6	450	
0.5%Pt+0.5%Au	2	76	94	0	4	380	
	1	84	92	0	8	420	
0.25%Pt+0.75%Au	2	86	89	1	10	430	
	1	83	85	1	14	415	
0.10/D	2	78	78	1	21	390	
0.1%Pt+0.9%Au	1	88	75	2	23	440	
10/4	2	54	67	5	28	270	
1%Au	1	36	62	6	32	180	

^a Reaction conditions: water (20 ml); 0.6 M 1,2-propanediol; 1,2-propanediol/total metal ratio = 2000; O₂ 3 bar; reaction temperature 60 °C; reaction time 4 h; TOF calculated

at 4 h on the basis of total metal loading; stirrer speed = 1000 rpm.

^b NaOH:substrate molar ratio.

surface area, and we consider this parameter might be important in determining the dispersion of the Au–Pt supported nanoparticles. Moreover, a higher pore volume will facilitate the accessibility of the substrate to the Au–Pt active site and lead to higher activity. However, the surface area and pore volume of the KB and KB-B supports are similar (Table 1), yet the KB-B-supported catalyst gives a slightly enhanced conversion, which implies that additional factors other than surface area and pore volume are also involved, probably more related to the surface structure/chemistry of the carbon. The KB-B activated carbon was used in all subsequent experiments.

3.2. The effect of the metal on catalyst performance

A series of monometallic Au, Pd, Pt and bimetallic Au–Pd, Au–Pt and Pd–Pt colloids were prepared and immobilised on the KB-B activated carbon. Comparison of the catalytic activity of Au, Pd and Pt supported catalysts (Table 3) showed that the Au catalyst was superior with respect to the monometallic Pd and Pt catalysts. Combining Pd or Pt with Au resulted in a significant increase in conversion for the bimetallic supported Au–Pd and Au–Pt nanoparticles by a factor of 1.5–2.5, whereas a Pd–Pt catalyst showed a decrease in conversion with respect to the monometallic Au catalyst. Nevertheless, it is evident that the bimetallic Pd–Pt catalysts showed enhanced conversion with respect to the monometallic Pd and Pt catalysts. An enhancement in the selectivity to lactate was also observed with the utilisation of Au–Pd or Au–Pt catalysts.

Table 5

Effect of AuPt bimetallic catalyst	loading on the selective of	oxidation of 1,2 propane diol at 30 °C	a
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Catalyst	NaOH/S ^b	Conversion (%)	Selectivity (%)			
			Lactate	Formate	Acetate	$TOF(h^{-1})$
19/04	2	<1	-	-	-	-
1%Pt	NaOH/Sb Conversion (%) Selectivity Lactate 2 <1	-	-	-	-	
	2	24	96	0	4	120
0.95%Pt+0.05%Au	1	30	93	1	6	150
0.0%Dt + 0.1%Au	2	55	93	2	5	275
0.9%Pt+0.1%Au	1	60	90	2	8	300
0.75%Pt + 0.25%Au	2	58	93	2	5	290
	1	65	89	2	9	325
	2	69	92	2	6	345
0.5%Pt + 0.5%Au	1	73	83	3	14	365
0.25%04 + 0.75% 4.4	2	59	80	2	18	295
0.25%Pt+0.75%Au	1	66	71	4	25	330
0.1%Pt+0.9%Au	2	48	62	2	36	240
	1	61	60	3	37	305
	2	35	56	5	39	175
0.05%Pt+0.95%Au	1	24	48	5	47	120
19/ 4	2	30	50	5	45	150
1%Au	1	18	49	4	47	90

^a *Reaction conditions*: water (20 ml); 0.6 M 1,2-propanediol; 1,2-propanediol/total metal ratio = 2000; O₂ 3 bar; reaction temperature 30 °C; reaction time 4 h; TOF calculated at 4 h on the basis of total metal loading; stirrer speed = 1000 rpm.

^b NaOH:substrate molar ratio.

Table 6

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Effect of base identit	v on the selective	oxidation of 1.2-	Dropanediol using	a I wt.%Au–Pt	carbon catalyst."
	J	· · · · · · ·			

Base	Conversion (%)	Selectivity (%)	Selectivity (%)					
		Lactate	Formate	Acetate	Pyruvate	Hydroxy-acetone		
LiOH	80	85	4	11	0	0	800	
NaOH	78	86	3	11	0	0	780	
KOH	69	85	3	12	0	0	690	
RbOH	66	88	3	9	0	0	660	
CsOH	53	89	3	8	0	0	530	

^a Reaction conditions: 1,2-propanediol (0.6 mol); 1,2-propanediol/total metal ratio=4000; base/1,2-propanediol molar ratio=1; reaction temperature 40°C; O₂ 3 bar; reaction time 4 h.

The effect of base employed was studied and it was found that in the case of Au and Au–Pd catalysts an increase in base concentration was accompanied by an increase in conversion, which is in good agreement with previous reports [16,17,21]. However, in



Fig. 1. Oxidation of 1,2-propanediol with air using the 0.5%Au+0.5%Pt/KB-B catalyst. *Reaction conditions*: water (100 ml); 1,2-propanediol (0.6 M); NaOH/1,2-propanediol molar ratio=1; 1,2-propanediol/total metal ratio=5000; reaction time=30–120 min; stirrer speed = 1000 rpm. *Key*: (\blacklozenge) 1,2-propanediol conversion; (\blacksquare) lactate selectivity.

the case of Au–Pt catalysts, an increase in base concentration was accompanied by a significant *decrease* in conversion. One possible explanation for this effect may be the coverage of Au–Pt active sites by sodium ions, leading to the observed decrease in conversion. However, in addition, it should be noted that differences in surface concentrations of Pd and Pt and their relative stabilities under 3 bar of oxygen and the basic reaction conditions could also play a significant role. The electrode potentials for Au, Pd and Pt at different pH values [31] indicate that Au is stable under the basic reaction conditions used (*i.e.* $pH \sim 10$), whereas Pd and Pt can be partially converted to their corresponding oxides and hydroxides, which might also correlate with the observed decrease in activity for catalysts based on these metals.

Taking into account the fact that the Au-Pt catalyst showed higher catalytic activity than the Au-Pd catalyst, a systematic study of the Au-Pt weight ratio was carried out at a reaction temperature of 60°C, as shown in Table 4. Addition of a small amount of Au (0.05 wt%) to Pt increased the activity significantly (based on turnover frequency (TOF)), and by further increasing the Au content a progressive increase in conversion was observed, with a maximum being attained for 0.25 wt%Au. However, choosing a Au content in the 0.5-0.75 wt% range led to a slight decrease in catalytic activity, although at the highest Au loading of 0.9 wt% the activity was restored. These results demonstrate the beneficial effect of mixing gold with platinum and by selecting the appropriate Au/Pt ratio the catalytic activity could be tuned. Moreover, the significant activity observed at low Au or Pt loadings suggest that a dilute amount of either Au-in-Pt or Pt-in-Au is highly desirable for achieving high activity, as has been observed previously in the case of the Au-Pd bimetallic catalyst system [32]. Our



Fig. 2. XPS spectra of the monometallic Au, Pd and Pt catalysts supported on KB-B carbon (all spectra normalised to the same intensity).

catalytic results also show that there is a distinct enhancement in the selectivity to lactic acid with increasing Pt content. The effect of the NaOH/1,2-propanediol ratio was also studied, and it is clear that a lower selectivity to lactate was observed at lower NaOH/1,2propanediol molar ratios with these Au–Pt catalysts. It is interesting that the effect of the NaOH/1,2-propanediol ratio was different for the two AuPt catalysts (Table 3) and the catalyst becomes more active at lower concentrations of base. Indeed, we have shown recently [36] that supported AuPt catalysts can be highly effective for the oxidation of glycerol under base-free conditions.

The effect of reaction temperature was also investigated in this study and the same series of catalysts were tested at 30° C (Table 5). A lower reaction temperature was found to be beneficial for the formation of lactate, as the generation of acetate and

Table 7

XPS characterisation of Au, Pd, Pt, Au-Pd and Au-Pt nanoparticles supported on C.



Fig. 3. XPS spectra of the bimetallic AuPt, PdPt and AuPd catalysts supported on KB-B carbon.

formate decreased significantly. Moreover, in terms of activity, the beneficial effect of alloying Au and Pt is evident.

3.3. Effect of base identity on catalyst performance

To investigate the effect of the counter cation for the hydroxide base, experiments were carried out on the oxidation of 1,2propanediol with the 1 wt%Au–Pt/KB-B catalyst (Au:Pt=1:1). The bases investigated were LiOH, NaOH, KOH, RbOH and CsOH and the results are presented in Table 6. The conversion of 1,2-propanediol decreased as the size of the alkali metal ion increased, indicating

Sample	BE Au 4f _{7/2}	BE Pt 4f _{7/2}	BE Pd 3d _{5/2}	At%Au	At%Pt	At%Pd
0.5%Au+0.5%Pt/KB-B	84.1	71.5	0	1.03	1.31	0
0.5%Pd + 0.5%Pt/KB-B	0	71.7	335.7	0	1.50	0.77
0.5%Au + 0.5%Pd/KB-B	84.0	0	335.7	1.07	0	1.34
1%Au/KB-B	84.2	0	0	2.29	0	0
1%Pd/KB-B	0	0	335.6	0	0	1.39
1%Pt/KB-B	0	71.4	0	0	0.31	0
0.5%Au+0.5%/Pt/KB	84.1	71.8	0	0.82	1.38	0
0.5%Au+0.5%Pt/G-60	84.1	71.5	0	0.73	0.73	0



Fig. 4. (a) High angle angular dark field (HAADF) STEM image and (b) the corresponding particle size distribution of the 0.5%Au+0.5%Pt/KB-B catalyst sample; (c) HAADF image of an individual metal particle and (d) its corresponding XEDS spectrum confirming that it is a AuPt alloy.

that LiOH, NaOH and KOH are better choices of base for this particular reaction. This effect may possibly be due to the larger cations being adsorbed on the catalyst surface leading to a loss of active surface area.

3.4. Oxidation of 1,2-propanediol with air

To further decrease the environmental impact of this reaction, studies were carried out using air as oxidant in place of pure oxygen. With a substrate-to-metal ratio of 5000, a conversion of *ca.* 40% was achieved after 2 h of reaction (Fig. 1). The selectivity towards lactate (81% at 38% conversion) was decreased in comparison with equivalent reactions in pure oxygen; however, the use of air in this system represents a significant simplification of the overall reaction process that makes it well worthy of further investigation.

3.5. Characterisation of the catalysts

The catalysts were characterised using XPS and transmission electron microscopy and the studies presented here are additional to those published previously [33,34]. Using these techniques it is possible to determine the surface ratios of the metal and the surface oxidation states along with the morphology of the supported nanoparticles. Results of the XPS characterisation of the carbon supported nanoparticles are shown in Table 7 and Figs. 2 and 3. These data indicate that all the Au species are present in the metallic state as inferred by a Au($4f_{7/2}$) binding energy of *ca*. 84 eV, irrespective of whether they are present in the mono- or bi-metallic systems. Similarly, the reported Pt($4f_{7/2}$) energies (*ca*. 71.5 eV) are slightly higher than expected for metallic Pt (71.1 eV), however, we consider this is consistent with the nanoparticulate nature of the metal, since the effect of final state effects gives an apparent higher binding energy in the small nanoparticles when compared with the bulk material. For the monometallic catalyst the $Pd(3d_{5/2})$ energies are observed to be around 335.7 eV and this is intermediate to the energies of Pd(0) (334.8 eV) and Pd(II) (336.8 in PdO) [35]. This has been ascribed in the past to both PdO or metallic Pd, a definite shoulder to the monometallic Pd catalyst at *ca*. 337 eV is a clear indication that PdO is present in these nanoparticles, along with metallic Pd as evidenced by the main intensity of the signal at 335.7 eV (Fig. 2), this binding energy being consistent with the work of Rodriguez [36] where a shift of *ca*. +0.7 eV is considered indicative of Pd alloying. However, there is no evidence for PdO being present in the bimetallic catalysts. Molar ratios for the Pt/Au and Pd/Au supported on the KB-B carbon are found to be 1.25 (expected 1/1) and 1.25 (1.85 expected) respectively.

The Au-Pd supported nanoparticles prepared using the solimmobilisation method have been extensively characterised by STEM-HAADF analysis, and the results have been reported in detail elsewhere. [33,34]. The Au-Pd nanoparticles are in fact random alloys, have particle sizes in the 2-5 nm range, and typically display a narrow particle size distribution. Fig. 4(a) shows an HAADF image of the sol-immobilised 0.5%Au+0.5%Pt/KB-B carbon catalyst sample. The corresponding particle size distribution which is presented in Fig. 4(b), shows that the mean particle diameter is 2.1 nm, and nearly all the particles are below 5 nm in size. This mean particle size is much smaller than that observed for AuPd/carbon catalyst which has a mean particle size of 3.7 nm [33,34]. The higher magnification image of an individual metal particle shown in Fig. 4(c)is typical of this sample and shows an f.c.c. type structure. Furthermore, the co-existence of the Au L_{α} and Pt L_{α} peaks in the corresponding XEDS spectrum from this particle (Fig. 4(d)) confirms that it is indeed a AuPt alloy.

Based on the characterisation presented it is apparent that in the AuPt and AuPd catalysts the metals are present in the zero valent state and they have the same surface atomic ratios of the metals. The difference in activity can be ascribed to the smaller mean particle size of the AuPt nanoparticles (2.1 nm) as compared with the AuPd nanoparticles (3.7 nm [33,34]) as more of the metal is therefore present on the surface in the AuPt catalysts.

4. Conclusions

The use of Au–Pd nanoalloys supported on activated carbon prepared using a sol-immobilisation method is observed to enhance the selective oxidation of 1,2-propanediol significantly under mild reaction conditions. The alloying of gold with platinum leads to a catalyst which is significantly more active than gold alloyed with palladium under the reported conditions. It has been shown that the reaction can be carried out under significantly milder conditions than have been previously reported for this oxidation [21,30], with significant reduction of the mass of the catalyst used; additionally, air can be used as the oxidant. The enhanced activity of the supported AuPt catalysts as compared to the AuPd catalysts is considered to be due to the AuPt nanoparticles having a considerably smaller mean particle size which leads to more active metal being present on the surface.

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