Solvent-free oxidation of benzyl alcohol using Au–Pd catalysts prepared by sol immobilisation

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We report the preparation of Au–Pd nanocrystalline catalysts supported on TiO_2 and carbon prepared *via* a sol-immobilisation technique using three different preparation strategies; namely, simultaneous formation of the sols for both metals or initial formation of a seed sol of one of the metals followed by a separate step in which a coating sol of the second metal is added. The catalysts have been structurally characterised using a combination of transmission electron microscopy and X-ray photoelectron spectroscopy. The catalysts have been evaluated for the oxidation of benzyl alcohol under solvent-free conditions. The catalysts prepared using the sol immobilisation technique show higher activity when compared with catalysts prepared by impregnation, particularly as lower metal concentrations can be used. The Au–Pd catalysts were all more active than the corresponding monometallic supported Au or Pd catalysts. For 1 wt% Au–Pd/TiO_2 the order of metal addition in the preparation was not observed to be significant with respect to selectivity or activity. However, the 1 wt% Au–Pd/carbon catalysts are more active but less selective to benzaldehyde than the TiO_2-supported catalysts when compared at iso-conversion. Furthermore, for the carbon-supported catalyst the order of metal addition has a very marked affect on activity. The carbon-supported catalysts are also more significantly affected by heat treatment, *e.g.* calcination at 400 °C leads to the activity being decreased by an order of magnitude, whereas the TiO_2-supported catalysts show a 50% decrease in activity. Toluene is observed as a by-product of the reaction and conditions have been identified that minimise its formation. It is proposed that toluene and benzaldehyde are formed by competing parallel reactions of the initial benzyl intermediate *via* an adsorbed benzylidene species that can either be hydrogenated or oxidised. Hence, conditions that maximise the availability of oxygen on the catalyst surface favour the synthesis of benzaldehyde.

Introduction

There is a continued interest in gold nanoparticles as catalysts for a broad range of selective chemical transformations.[1–7] These include the low temperature oxidation of CO,[8] especially when used as part of the processes for purifying a fuel cell feedstock,[9,10] the synthesis of vinyl chloride by the hydrochlorination of ethyne,[11] the selective oxidation of alkenes to epoxides[12,13] and alcohols to aldehydes[14] as well as selective hydrogenation.[15] Part of this intense fascination with gold chemistry at the nanoscale is the very wide range of new applications for gold as a catalyst that are being discovered on a regular basis. Furthermore, since gold is considered to be the most noble of metals these observations arouse the interest of many scientists interested in discovering the origins of this enhanced catalytic activity at the nanoscale.

Against the background of this diverse catalytic chemistry that has been discovered for pure gold nanoparticles, we have recently shown that the combination of gold with palladium leads to enhanced catalytic activity and selectivity in redox processes. While gold alone is a very effective catalyst for the selective oxidation of an alcohol to an aldehyde under solvent free conditions,[14] the alloying of gold with palladium leads to a twenty five-fold enhancement in activity with simultaneous retention of selectivity.[16] While palladium alone is an exceptionally effective catalyst for the direct hydrogenation of molecular oxygen to produce hydrogen peroxide,[17] the alloying of gold with the palladium significantly enhances the activity and selectivity.[18–23] These two specific reactions demonstrate that gold–palladium alloy nanoparticles can give enhanced reactivity over monometallic gold and palladium alone, although it should be noted that this enhancement is not a universal feature for the oxidation of alcohols. In our early studies[16,18–23] we used a relatively straightforward wet co-impregnation method to prepare gold–palladium nanoparticles that were either homogeneous alloys[23] or core-shell structures.[22] Subsequently,[24] we recently showed that catalysts with enhanced activity can be prepared using a

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sol-immobilisation method, and in this paper we continue to investigate the advantages of this new alternative methodology, specifically for the oxidation of benzyl alcohol as a model substrate.

The oxidation of primary alcohols to aldehydes is an important laboratory and commercial procedure.[25–27] Aldehydes are valuable both as intermediates and as high value components for the perfume industry.[25] Often oxidations of this type are carried out using stoichiometric oxygen donors such as chromate or permanganate, but these reagents are expensive and have serious toxicity and environmental issues associated with them.[27] Given these limitations, there is substantial interest in the development of heterogeneous catalysts that use molecular O_2 as the oxidant. Au nanocrystals have been shown to be highly effective for the oxidation of alcohols with O_2 in an aqueous base, in particular diols and triols; although under these conditions, the product is the corresponding mono-acid, not the aldehyde.[28–30] However, gold in the absence of base has recently been shown to be highly effective for the oxidation of alcohols,[14] and when alloyed with palladium can give enhanced activity under solvent free conditions.[16] The observation of high activity using molecular oxygen under solvent free conditions is of particular importance for the transformation of alcohols using a green chemistry approach. In our previous work, we demonstrated that the combination of gold and palladium could provide a further pronounced enhancement in activity when the two metals are deposited together by sol-immobilisation.[24] In this paper we extend this approach to investigate whether or not the activity can be further enhanced by modifying the precise order in which the sols of the two metals are formed before immobilisation onto the support. In addition, in the oxidation of benzyl alcohol we observe toluene as a by-product[24] and in this paper we investigate how to minimize toluene formation.

Experimental

Catalyst preparation

Sol-immobilisation method. Three methods were used to prepare sol immobilised Au–Pd catalysts based on the sequence of metal addition and reduction. For the preparation of (Au–Pd)/support materials an aqueous solution of $PdCl_2$ (Johnson Matthey) and $HAuCl_4{\cdot}3H_2O$ (Johnson Matthey) of the desired concentration were prepared. Polyvinylalcohol (PVA) (1 wt% aqueous solution, Aldrich, MW = 10 000, 80% hydrolyzed) and an aqueous solution of $NaBH_4$ (0.1 M) were also prepared.

(a) Au + Pd sol. To an aqueous $PdCl_2$ and $HAuCl_4$ solution of the desired concentration, the required amount of a PVA solution (1 wt%) was added (PVA/(Au + Pd) (wt/wt) = 1.2); a freshly prepared solution of $NaBH_4$ (0.1 M, $NaBH_4$/(Au + Pd) (mol/mol) = 5) was then added to form a dark-brown sol.

(b) Pd@Au sol. To an aqueous $HAuCl_4$ solution of the desired concentration the required amount of a PVA solution (1 wt%) was added (PVA/(Au + Pd) (wt/wt) = 1.2); a freshly prepared solution of $NaBH_4$ (0.1 M, $NaBH_4$/Au (mol/mol) = 5) was then added to form a red sol. The solution was stirred for 30 minutes. Then, the required amount of the stock aqueous $PdCl_2$ solution was added, followed by the desired amount of $NaBH_4$ ($NaBH_4$/Pd (mol/mol) = 5), obtaining a dark brown sol. The solution was stirred for a further 30 minutes.

(c) Au@Pd sol. To an aqueous $PdCl_2$ solution of the desired concentration the required amount of a PVA solution (1 wt%) was added (PVA/(Au + Pd) (wt/wt) = 1.2); a 0.1 M freshly prepared solution of $NaBH_4$ ($NaBH_4$/Pd (mol/mol) = 5) was then added to form a brown sol. The solution was stirred for 30 minutes. Then, the desired amount of the stock $HAuCl_4$ aqueous solution was added, followed by the desired amount of $NaBH_4$ ($NaBH_4$/Au (mol/mol) = 5), obtaining a dark brown sol. The solution was stirred for a further 30 minutes.

Two supports have been used, namely, TiO_2 (Degussa P25) and carbon (Darco G60, Aldrich). After 30 min of sol generation, the colloid was immobilised by adding activated carbon or titania (acidified at pH 1 by sulfuric acid) under vigorous stirring conditions. The amount of support material required was calculated so as to have a total final metal loading of 1% wt. The metal ratio for the 1 wt% Au + Pd/TiO_2 catalyst was 1:1 molar (we selected the Au + Pd/TiO_2 catalyst with 1:1 by wt loading so that it was comparable with catalysts prepared previously by impregnation[16]). For all other catalysts a 1:1 wt ratio was used (Pd:Au = 2:1 molar). After 2 h the slurry was filtered, the catalyst washed thoroughly with distilled water (neutral mother liquors) and dried at 120 °C overnight. The calcined catalysts were pre-treated at 400 °C under static air for 3 h.

Impregnation method. 1 wt% Pd-only, 1 wt% Au-only and Au–Pd bimetallic catalysts were prepared by impregnation of carbon (Darco G60, Aldrich) or TiO_2 (Degussa P25), *via* an impregnation method using aqueous solutions of $PdCl_2$ (Johnson Matthey) and/or $HAuCl_4{\cdot}3H_2O$ (Johnson Matthey). For the 0.5%Au–0.5%Pd/carbon catalyst, the detailed preparation procedure employed is described below. An aqueous solution of $HAuCl_4{\cdot}3H_2O$ (2 ml, 5 g dissolved in water (250 ml)) and an aqueous solution of $PdCl_2$ (0.83 ml, 1 g in water (25 ml)) were simultaneously added to carbon (3.8 g). The paste formed was ground and dried at 110 °C for 16 h and calcined in static air, typically at 400 °C for 3 h.

Benzyl alcohol oxidation

Benzyl alcohol oxidation was carried out in a stirred reactor (100 mL, Autoclave Engineers Inline MagneDrive III). The vessel was charged with alcohol (40 mL) and catalyst (0.1 g). The autoclave was then purged 5 times with oxygen leaving the vessel at 10 bar gauge. The stirrer was set at 1500 r.p.m. and the reaction mixture was raised to the required temperature and the reaction time was started when the required reaction time was reached. Samples from the reactor were taken periodically, *via* a sampling system. For the analysis of the products a GC-MS and GC (a Varian star 3400 cx with a 30 m CP-Wax 52 CB column) were employed. The products were identified by comparison with known standards. For the quantification of the amounts of reactants consumed and products generated, the external calibration method was used.

Catalyst characterisation

Samples for examination by transmission electron microscopy (TEM) were prepared by dispersing the catalyst powder in high purity ethanol, then allowing a drop of the suspension to evaporate on a holey carbon film supported by a 300 mesh copper TEM grid. Samples were then subjected to bright field diffraction contrast imaging experiments in order to determine particle size distributions. The instrument used for this analysis was a JEOL 2000FX TEM operating at 200 kV.

X-Ray photoelectron spectra were recorded on a Kratos Axis Ultra DLD spectrometer employing a monochromatic AlK(X-ray source (75–150 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.

Results and discussion

Oxidation of benzyl alcohol with Au + Pd/TiO_2

The effect of the reaction conditions on the oxidation of benzyl alcohol was investigated using 1 wt% Au + Pd/TiO_2. First the effect of catalyst mass was investigated using the same reaction conditions (120 °C, P_{O2} 10.2 bar, stirring rate 1500 r.p.m., 2 h reaction time). In the absence of catalyst no conversion was observed. Increasing the catalyst mass up to 100 mg had a linear effect on the benzyl alcohol conversion and turn over frequency (TOF) remained constant (Fig. 1), indicating that in this range no diffusion limitations were apparent. Product selectivity is affected by catalyst loadings above 50 mg, and benzaldehyde and toluene are the major products, while benzoic acid and benzyl benzoate are formed in minor amounts. Benzaldehyde selectivity decreases as the catalyst mass is increased, and this is coupled with a higher selectivity to toluene. This is confirmed by data at iso-conversion of benzyl alcohol (10%) which show these trends clearly (Table 1). At higher catalyst mass a slight decrease in TOF was apparent indicating that diffusion limitations were present, hence in subsequent experiments a catalyst mass of 100 mg was used as standard. We then investigated the effect of stirring rate and oxygen pressure. The reactions are carried out in a stirred autoclave reactor and involve a three phase system (solid catalyst, liquid and gas phase reactants) and the oxygen has to dissolve in the benzyl alcohol and the solubility will be influenced by these parameters. Increasing the stirring rate will increase the mixing between the liquid and gas phases in the reaction mixture and this will increase the availability of oxygen at the catalyst surface. Consequently, increasing the stirring rate increased the rate of reaction (Fig. 2) and at the highest stirring rate possible with the autoclave reactor we have used, *i.e.* 1500 rpm, the selectivity of benzaldehyde was highest. The highest increase in rate was observed when the stirring rate was increased from 250 rpm (TOF 5850 h^{-1}) to 500 rpm (TOF 10 000 h^{-1}). Interestingly, the selectivity to benzaldehyde was higher at the lower stirring speed and the selectivity to benzaldehyde steadily increased with stirring speed above 500 rpm (Fig. 2). Data at iso-conversion confirm this observation (Table 2). By combining the selectivities at different stirring speeds with the TOF-values one is able to see the contributions of the two pathways to the total turnover as a function of stirring. This reveals that the toluene contribution quickly rises to *ca.* 4000 h^{-1} at 500 rpm and stays constant thereafter, while the TOF for benzaldehyde pathway increases continuously and, interestingly, in proportion to the square root of the stirring speed. We consider this behaviour to be similar to that observed for forced convection to a planar surface (*cf.* the square root dependence of current on rotation speed using a rotating disc electrode). We therefore propose that toluene formation arises wholly from reaction of adsorbed species on the surface, while oxidation involves oxygen that is not adsorbed but reacts with a suitable intermediate at the surface.

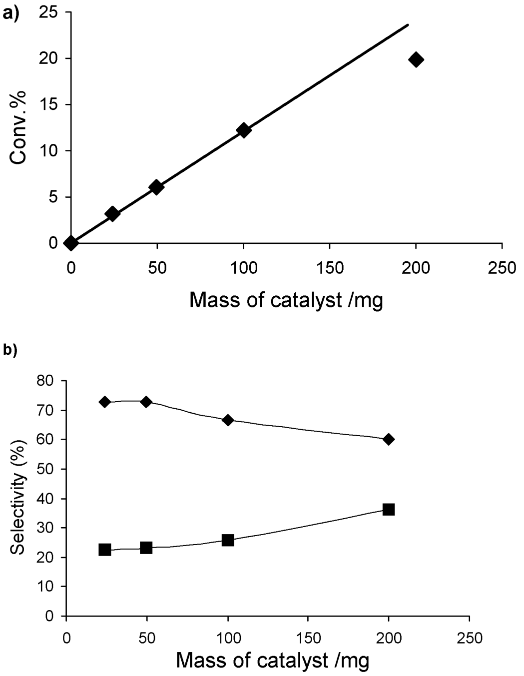

Fig. 1 Effect of catalyst loading on benzyl alcohol oxidation with 1 wt% Au + Pd/TiO_2: (a) conversion and (b) selectivity, Key: ◆ benzaldehyde, ■ toluene. Reaction conditions: 120 °C, P_{O2} = 10.2 bar, stirring rate 1500 rpm, 2 h reaction time.

We subsequently investigated the effect of oxygen partial pressure. There was no effect on rate but a marked increase in benzaldehyde selectivity was observed (Fig. 3). Data at iso-conversion of benzyl alcohol confirm these trends (Table 3). The oxygen partial pressure should, presumably, affect the equilibrium oxygen concentration in solution, so the absence of any effect implies that oxygen, whose availability is controlled by the stirring speed, very rapidly reacts with surface-adsorbed species. Hence the reaction is zero order in oxygen and the initial activation of benzyl alcohol on the catalyst surface does not depend on the partial pressure of oxygen; however, the subsequent formation of either benzaldehyde or toluene is heavily dependent on the concentration of oxygen at the surface. The formation of the products

Table 1 Effect of catalyst loading in the benzyl alcohol oxidation at iso-conversion with the dried 1 wt% (Au + Pd)/TiO_2 catalyst prepared by sol immobilisation[a]

		Selectivity (%)						
Catalyst weight/mg	Conv. (%)	Benzene	Toluene	Benzaldehyde	Benzoic acid	Benzyl benzoate	Acetal	TOF/h^{-1}[b]
24	10	3.3	22.4	72.8	0.8	0.7	0	14 860
50	10	1.1	23.1	72.8	1.3	1.7	0	14 330
100	10	6.3	25.9	66.6	0.6	0.6	0	14 280
200	10	1.3	36.1	60.2	1.2	1.2	0	11 630

[a] Reaction conditions: benzyl alcohol, 0.1–0.2 g of catalyst, T = 120 °C, pO_2 = 150 psi, stirring rate 1500 rpm. [b] Calculation of TOF (h^{-1}) after 0.5 h of reaction. TOF numbers were calculated on the basis of total loading of metals.

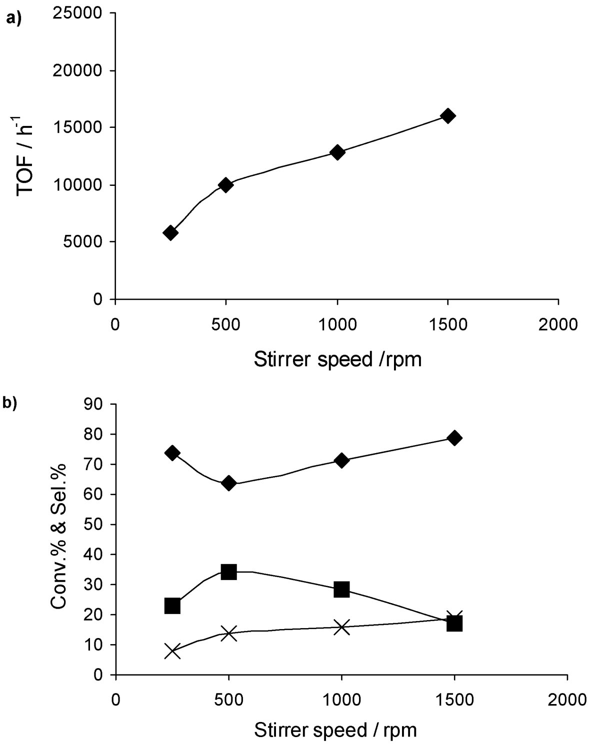

Fig. 2 Effect of stirring speed on benzyl alcohol oxidation with 1 wt% Au + Pd/TiO_2: (a) turn over frequency and (b) conversion and selectivity, Key: × conversion, ◆ benzaldehyde and ■ toluene. Reaction conditions: 120 °C, P_{O2} = 10.2 bar, 100 mg of catalyst, 2 h reaction time.

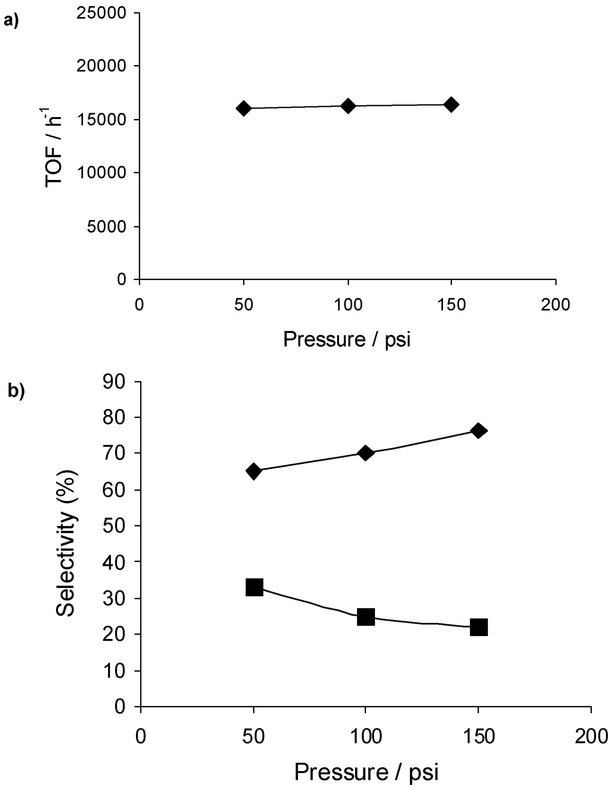

Fig. 3 Effect of oxygen pressure on benzyl alcohol oxidation with 1 wt% Au + Pd/TiO_2: (a) turn over frequency and (b) selectivity, Key: ◆ benzaldehyde and ■ toluene. Reaction conditions: 120 °C, stirring rate 1500 rpm, 100 mg of catalyst, 2 h reaction time.

can, therefore, be rationalised in terms of a series of pathways (Fig. 4). It is considered that benzyl alcohol initially adsorbs dissociatively on the surface of the metal nanoparticles giving benzyl and hydroxyl intermediates. The benzyl surface species is further dehydrogenated to give a surface benzylidene species and surface adsorbed hydrogen atoms. The benzylidene then

Table 2 Effect of stirring speed in the benzyl alcohol oxidation at iso-conversion with the dried 1 wt%(Au + Pd)/TiO_2 catalyst prepared by sol immobilisation[a]

		Selectivity (%)						
Stirring speed/rpm	Conv. (%)	Benzene	Toluene	Benzaldehyde	Benzoic acid	Benzyl benzoate	Acetal	TOF/h^{-1}[b]
250	10	0.7	23.8	73.3	1.3	0.9	0	5850
500	10	0.3	34.4	63.5	0.8	1.0	0	10 030
1000	10	0.0	29.7	68.1	0.6	1.6	0	12 830
1500	10	0.5	22.2	76.3	0.4	0.7	0	16 060

[a] Reaction conditions: benzyl alcohol, 0.05 g of catalyst, T = 120 °C, pO_2 = 150 psi, stirring rate 250–1500 rpm. [b] Calculation of TOF (h^{-1}) after 0.5 h of reaction. TOF numbers were calculated on the basis of total loading of metals.

Table 3 Effect of pressure in the benzyl alcohol oxidation at iso-conversion with the dried 1 wt%(Au + Pd)/TiO_2 catalyst prepared by sol immobilisation[a]

		Selectivity (%)						
Pressure/psi	Conv. (%)	Benzene	Toluene	Benzaldehyde	Benzoic acid	Benzyl benzoate	Acetal	TOF/h^{-1}[b]
50	10	0.4	33.0	65.0	0.7	0.9	0	16 010
100	10	0.6	24.8	70.1	1.8	2.7	0	16 250
150	10	0.5	22.0	76.2	0.5	0.8	0	16 420

[a] Reaction conditions: benzyl alcohol, 0.05 g of catalyst, T = 120 °C, pO_2 = 50–150 psi, stirring rate 1500 rpm. [b] Calculation of TOF (h^{-1}) after 0.5 h of reaction. TOF numbers were calculated on the basis of total loading of metals.

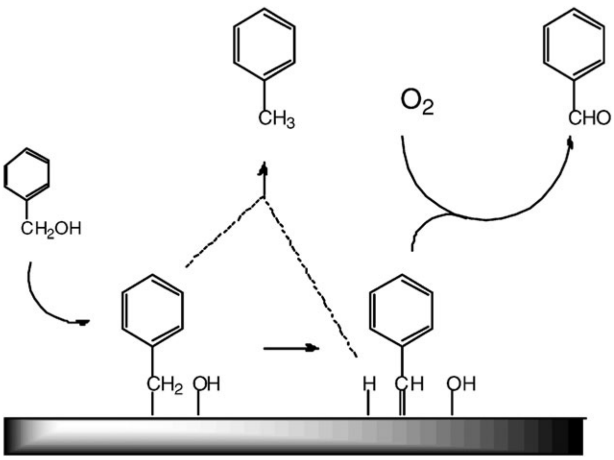

Fig. 4 Schematic representation of chemisorption of benzyl alcohol and subsequent formation of toluene in competition with oxidation to benzaldehyde.

reacts with O_2 to give benzaldehyde or the surface hydrogen reacts with either benzyl or benzylidene to give toluene. It is worth noting that the following exothermic chemical equation can be written:

$$2PhCH_2OH \rightarrow PhCH_3 + PhCHO + H_2O$$

In the absence of added oxygen therefore, toluene and benzaldehyde should be produced in equimolar amounts. This situation is most nearly achieved using catalysts supported on carbon that are not calcined. For TiO_2-supported catalysts, equimolar toluene and benzaldehyde is most closely attained at low oxygen pressures and low but, perhaps surprisingly, not the lowest stirring speeds.

The chemistry of the formation of benzaldehyde detailed in Fig. 4 deserves comment. Benzylidene generated in its ground triplet state, for example in the gas or liquid phases, in the presence of oxygen would be expected rapidly to form the carbonyl oxide, PhC–O–O (often represented as an ylid, $PhC{=}O^{+}{-}O^{-}$).[31] Carbonyl oxides are very reactive species; in competition with isomerisation to the dioxirane and dimerisation to the 1,2,4,5-tetroxane, reaction with benzyl alcohol would be expected to yield the hemiperacetal **1** and thence benzyl benzoate by dehydration, and reaction with benzaldehyde would yield stilbene ozonide **2**, a precursor of benzoic acid (Fig. 5). The presence of both benzyl benzoate and benzoic acid among the products of the reactions over supported Au–Pd catalysts, albeit with low selectivities, indicates the relevance of this chemistry in the heterogeneous situation but cannot be the main route to benzaldehyde. It seems plausible to suggest that, if the carbonyl oxide is indeed an intermediate, it is probably surface-bound, subsequently fragmenting to yield free benzaldehyde and an oxo-species on the surface, capable of generating a further molecule of benzaldehyde.

Hence the key factor controlling selectivity is the availability of oxygen at the catalyst surface. We tested this proposition by reacting benzyl alcohol in the absence of oxygen with a Au + Pd/TiO_2 catalyst prepared by impregnation. Toluene was observed when the reaction was carried out under equivalent reaction conditions and also toluene and benzaldehyde were observed in approximately equal amounts. In addition, if the catalyst has a marked dehydrogenation activity then the amount of surface hydrogen will be increased leading to higher toluene formation. The catalyst prepared from the addition of a Pd sol on a pre-formed Au sol (Pd@Au sol) resulted in a catalyst with enhanced hydrogenation/dehydrogenation activity and hence higher yields of toluene can be expected. This is consistent with the nanoparticle morphology as the surface of these particles can be expected to be rich in Pd which has a higher hydrogenation activity than Au. The catalysts prepared by sol immobilisation are more active than the 5 wt% Au + Pd/TiO_2 catalysts prepared by co-impregnation that we investigated previously.[16] However, the selectivity observed for toluene is significantly higher with the very active sol-immobilised catalysts, and this, we consider, is related to the higher hydrogenation activity for these catalysts.

An important factor that has to be considered for heterogeneous catalysts operating in a three phase system concerns catalyst stability.[32] One major problem is that the metallic components can leach into solution and this can lead either to a loss in catalyst activity on subsequent uses, or can enable the formation of an active homogeneous catalyst. Previously, we have shown that Au + Pd/TiO_2 catalysts prepared by co-impregnation are not stable when used as catalysts for the direct synthesis of hydrogen peroxide if they are not calcined at 400 °C.[22] This is due to significant loss of the Au and Pd which did not produce an active homogeneous species but did lead to significant loss in catalyst activity, and this was related to the structure of the Au–Pd alloy nanoparticles.[23] The effect of catalyst re-use was therefore investigated for the non calcined Au + Pd/TiO_2 catalyst (Table 4). These experiments were performed by initially reacting a 200 mg batch of the catalyst for 30 min (120 °C, 1500 r.p.m., P_{O2} 10.2 bar), recovering the material by filtration, washing the solid with acetone three times followed by drying (20 °C, 16 h). Unfortunately the amount of catalyst recovered was always

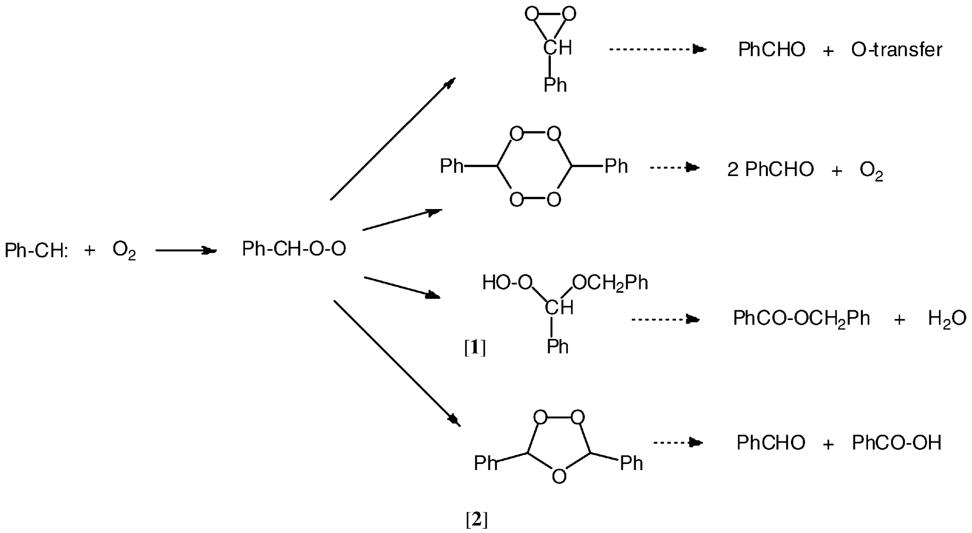

Fig. 5 Chemistry of carbonyl oxides in the gas or liquid phases.

Table 4 Recycling catalytic tests in the liquid phase oxidation of benzyl alcohol with a 1% (Au + Pd)/TiO_2 catalyst prepared by the sol immobilisation method[a]

		Selectivity (%)						
Number of uses	Conv. (%)	Benzene	Toluene	Benzaldehyde	Benzoic acid	Benzyl benzoate	Acetal	TOF/h^{-1}[b]
1st use	18.0	2.4	35.8	60.5	0.6	0.7	0	10 020
2nd use	14.3	2.0	32.5	64.1	0.7	0.8	0	7970
3rd use	12.9	3.2	32.4	62.9	0.7	0.8	0	7210
4th use	12.5	3.4	30.0	64.9	0.6	1.1	0	6960

[a] Reaction conditions: benzyl alcohol, 0.1–0.2 g of catalyst, T = 120 °C, pO_2 = 150 psi. [b] Calculation of TOF (h^{-1}) after 0.5 h of reaction. TOF numbers were calculated on the basis of total loading of metals.

lower than the initial amount used due to experimental losses in recovery/filtration and hence different masses of catalyst were used (Table 4). However, the TOF was constant within experimental error and consequently it is concluded that the uncalcined catalysts prepared using the sol-immobilisation method are stable and can be readily reused.

Investigation of the effect of order of metal addition

There are three ways in which the sol-immobilised catalysts can be prepared, *i.e.* the metals can be co-immobilised or either metal can be deposited first and the second in a subsequent step. Such methods can be expected to have significant effects on activity and selectivity as a result of the different structures that can be made. We have investigated this for TiO_2- and carbon-supported catalysts. For the TiO_2-supported catalysts (Table 5) the initial rate, as determined by TOF at 0.5 h reaction was highest for Pd@Au/TiO_2, with the order of activity being Pd@Au/TiO_2 > Au@Pd/TiO_2 > Pd + Au/TiO_2. When compared at 50% conversion all catalysts gave very similar selectivities but Pd + Au/TiO_2 did give a slightly higher toluene selectivity and this catalyst was the most active at 2 h reaction time (Table 6). For the carbon-supported catalysts the order of addition had a marked effect on the initial rate (Table 5), although all showed similar activity at 2 h reaction time (Table 5). Pd@Au/carbon was significantly more active than the other two catalysts based on TOF at 0.5 h reaction (Table 5) and the order of activity was observed to be Pd@Au/carbon > Au + Pd/carbon > Au@Pd/carbon. The carbon-supported catalysts were much more active by about a factor of two when compared with the TiO_2-supported catalysts (Tables 5 and 6), however, they were much less selective to benzaldehyde.

Effect of calcination on catalyst performance

The sol-immobilised catalysts were calcined at 400 °C and the activity was investigated for the oxidation of benzyl alcohol (catalyst 100 mg, 120 °C, 1500 r.p.m., P_{O2} 10.2 bar). The results show that both sets of catalysts are markedly affected by calcination, but the effect is far more significant for the carbon-supported catalysts, which decrease in activity by about an order of magnitude, whereas the TiO_2-supported catalysts halve in activity (Table 7). The calcined carbon-supported catalysts are all more selective for the synthesis of benzaldehyde, and comparison at iso-conversion shows that this is not just an effect of lower conversion and hence these calcined catalysts are more selective for partial oxidation (Table 8).

The activity of the 1 wt% Au + Pd/carbon catalyst prepared by sol-immobilisation and calcined at 400 °C could be compared with the Au–Pd catalysts prepared by co-impregnation that we have reported previously.[16] The sol-immobilised catalysts have a significantly higher activity (TOF 1780 h^{-1}) than the co-impregnated catalyst (TOF 490 h^{-1}).

Table 5 Benzyl alcohol oxidation results after 2 h reaction with Au–Pd catalysts supported on carbon and titania prepared by immobilisation method: effect of the order of metal reduction in the preparation[a]

		Selectivity (%)						
Catalyst	Conv. (%)	Benzene	Toluene	Benzaldehyde	Benzoic acid	Benzyl benzoate	Acetal	TOF/h^{-1b}
1% (Au + Pd)/TiO_2	61.2	0.5	26.7	69.2	1.7	1.9	0	15 360
1% (Pd@Au)/TiO_2	57.8	0.2	18.1	77.1	1.8	2.8	0	19 250
1% (Au@Pd)/TiO_2	48.7	0.4	23.0	72.3	1.9	2.5	0	17 360
1% (Au + Pd)/C	81.1	0.5	40.9	55.0	1.3	2.1	0.2	35 400
1% (Pd@Au)/C	70.4	0.4	35.1	62.6	2.0	0.0	0	41 930
1% (Au@Pd)/C	79.2	0.7	28.8	65.0	2.7	2.7	0	24 310

[a] Reaction conditions: benzyl alcohol, 0.1g of catalyst, T = 120 °C, pO_2 = 150 psi, stirring rate 1500 rpm. [b] Calculation of TOF (h^{-1}) after 0.5 h of reaction. TOF numbers were calculated on the basis of total loading of metals.

Table 6 Benzyl alcohol oxidation results at iso-conversion with Au–Pd catalysts supported on carbon and titania prepared by immobilisation method: effect of the order of metal reduction in the preparation[a]

		Selectivity (%)					
Catalyst	Conv. (%)	Benzene	Toluene	Benzaldehyde	Benzoic acid	Benzyl benzoate	Acetal
1% (Au + Pd)/TiO_2	50	0.5	26.9	69.1	1.5	2.0	0
1% (Pd@Au)/TiO_2	50	0.2	23.0	72.8	1.5	2.5	0
1% (Au@Pd)/TiO_2	50	0.4	23.0	72.2	1.9	2.5	0
1% (Au + Pd)/C	50	0.3	44.0	51.3	1.7	2.7	0.1
1% (Pd@Au)/C	50	0.3	41.6	54.6	1.6	1.8	0.1
1% (Au@Pd)/C	50	0.6	38.9	57.1	1.6	1.7	0.1

[a] Reaction conditions: benzyl alcohol, 0.1g of catalyst, T = 120 °C, pO_2 = 150 psi.

Table 7 Benzyl alcohol oxidation results after 2 h reaction with Au–Pd catalysts supported on carbon and titania prepared by immobilisation method and calcined at 400 °C in air: effect of the order of metal reduction in the preparation[a]

		Selectivity (%)						
Catalyst	Conv. (%)	Benzene	Toluene	Benzaldehyde	Benzoic acid	Benzyl benzoate	Acetal	TOF/h^{-1b}
1% (Au + Pd)/TiO_2	22.7	0.8	22.2	69.7	1.9	5.5	0	3940
1% (Pd@Au)/TiO_2	32.8	0.6	21.3	71.6	1.9	4.6	0	8650
1% (Au@Pd)/TiO_2	33.5	0.4	25.9	68.7	1.3	3.7	0	8780
1% (Au + Pd)/C	6.7	5.5	2.4	78.7	3.6	9.8	0	2490
1% (Pd@Au)/C	6.0	5.2	2.9	75.1	4.3	12.6	0	2430
1% (Au@Pd)/C	7.2	1.7	4.7	79.1	3.6	10.8	0	3410

[a] Reaction conditions: benzyl alcohol, 0.1g of catalyst, T = 120 °C, pO_2 = 150 psi, stirring rate 1500 rpm. [b] Calculation of TOF (h^{-1}) after 0.5 h of reaction. TOF numbers were calculated on the basis of total loading of metals.

Table 8 Benzyl alcohol oxidation results at iso-conversion with Au–Pd catalysts supported on carbon and titania prepared by immobilisation method: effect of the order of metal reduction in the preparation and catalyst pre-treatment[a]

			Selectivity (%)					
Catalyst	Catalyst pre-treatment	Conv. (%)	Benzene	Toluene	Benzaldehyde	Benzoic acid	Benzyl benzoate	Acetal
1% (Au + Pd)/C	Dried	5	0.2	44.2	54.9	0.6	0.1	0
1% (Pd@Au)/C	Dried	5	0.3	40.1	56.8	1.0	1.8	0
1% (Au@Pd)/C	Dried	5	0.6	35.2	59.5	1.4	3.3	0
1% (Au + Pd)/C	Calcined 400 °C/Air	5	6.1	3.6	76.1	3.5	10.6	0
1%Pd@Au/C	Calcined 400 °C/Air	5	6.8	3.4	73.7	4.1	12.0	0
1%Au@Pd/C	Calcined 400 °C/Air	5	2.2	4.3	85.1	2.1	6.3	0
1%Au + Pd/TiO_2	Dried	20	0.4	21.3	75.3	1.0	2.0	0
1%Pd@Au/TiO_2	Dried	20	0.3	33.1	63.8	0.9	1.9	0
1%Au@Pd/TiO_2	Dried	20	0.4	28.8	66.9	0.9	3.0	0
1%Au + Pd/TiO_2	Calcined 400 °C/Air	20	0.8	22.3	69.8	1.8	5.4	0
1%Pd@Au/TiO_2	Calcined 400 °C/Air	20	0.5	23.8	71.0	1.3	3.3	0
1%Au@Pd/TiO_2	Calcined 400 °C/Air	20	0.5	28.3	66.9	1.1	3.2	0

[a] Reaction conditions: benzyl alcohol, 0.1g of catalyst, T = 120 °C, pO_2 = 150 psi.

Characterisation of sol immobilised catalysts

TEM results. TEM has been used to characterise the particle size distributions for the 1 wt% Pd@Au, 1 wt% Au@Pd and 1 wt% AuPd sol-immobilised specimens on TiO_2, and carbon supports and the data are shown in Fig. 6 and 7, respectively. In all cases, the sol-immobilised particles are homogeneously dispersed over the support surfaces. Fig. 6 shows that the Pd@Au, Au@Pd and AuPd sols immobilised on TiO_2 have rather similar particle size distributions with median diameter values all in the 4.0–4.5 nm range. By comparison, (see Fig. 7) the Pd@Au and AuPd particle size distributions on carbon are a little larger at ~5.5 nm, and the Au@Pd on carbon are slightly smaller at 3.8 nm in diameter. It also interesting to note the Pd@Au, Au@Pd and AuPd alloy particles on TiO_2 all have a significantly narrower size distribution than their direct counterparts on carbon.

Fig. 8 shows the Pd@Au particle size distribution data on the TiO_2 and carbon supports after calcinations for 3 h at 400 °C. It is clear that the thermal stability of the Pd@Au alloy particles shows a strong dependence on support identity. On TiO_2 the Pd@Au particles exhibit some very limited

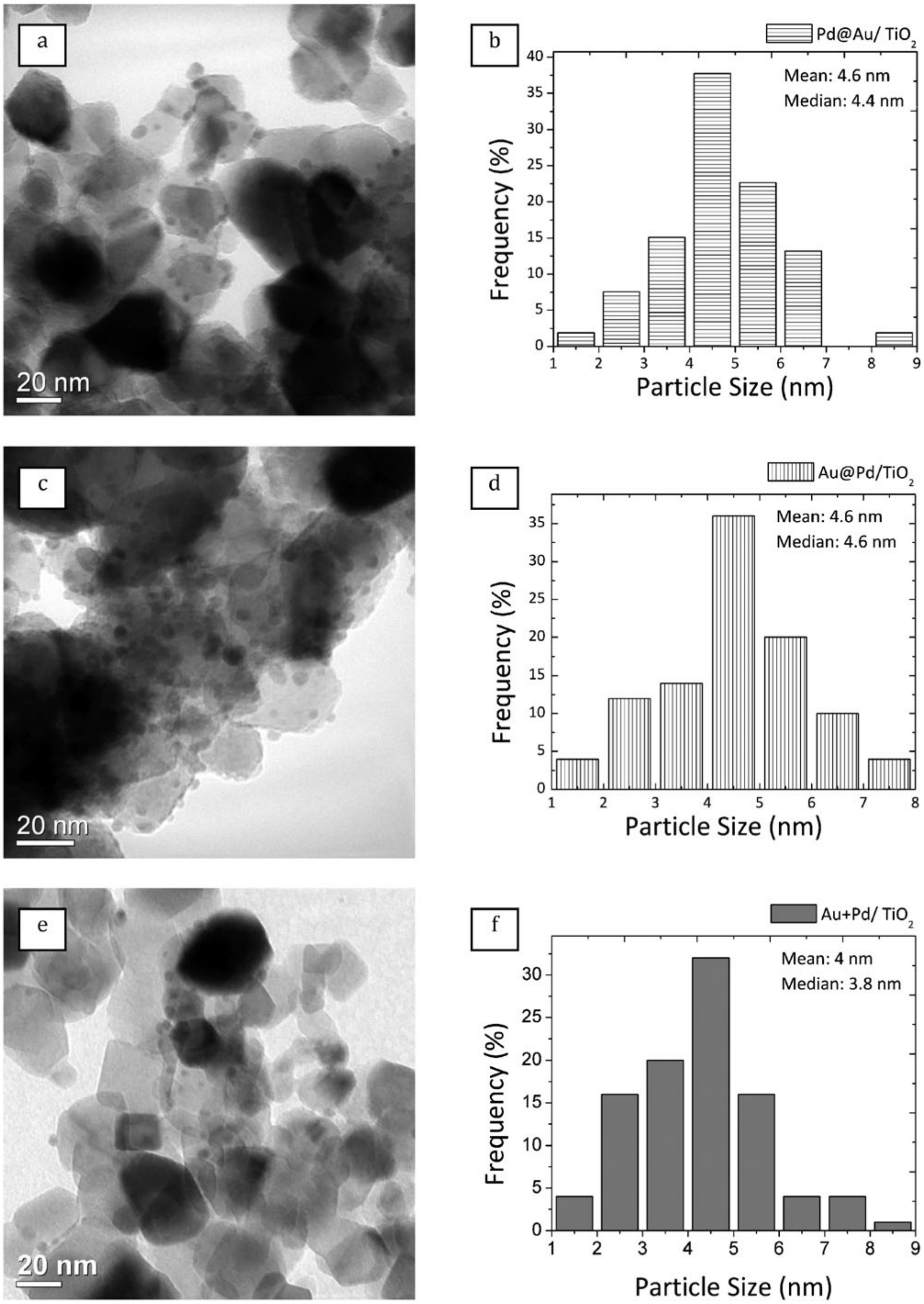

Fig. 6 Particle size distribution data, as determined from bright field TEM micrographs for the (a,b) 1 wt% Pd@Au/TiO_2,(c,d) 1 wt% Au@Pd/TiO_2 and (e,f) 1 wt% AuPd/ TiO_2 samples dried overnight at 120 °C.

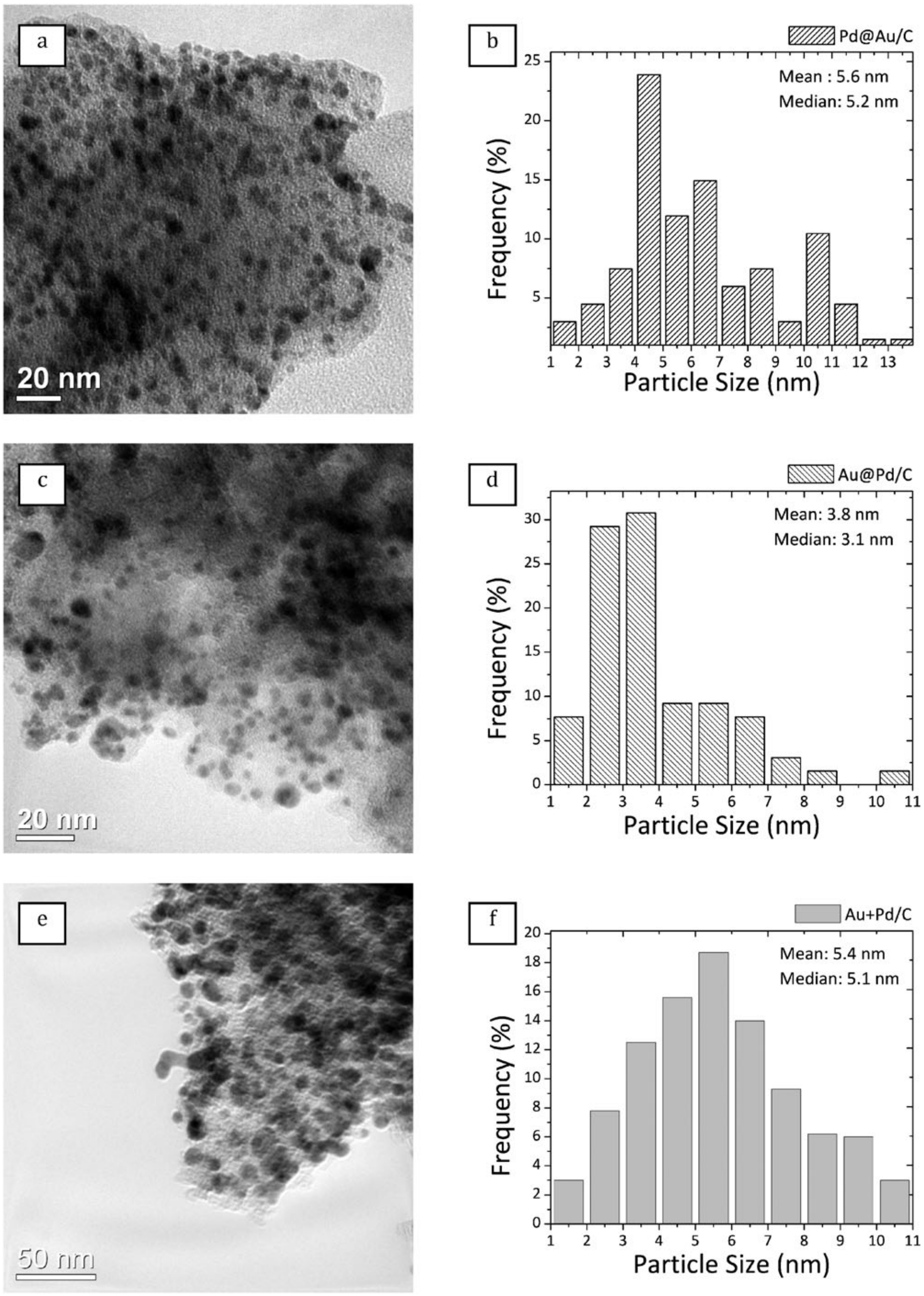

Fig. 7 Particle size distribution data, as determined from bright field TEM micrographs for the (a,b) 1 wt% Pd@Au/C, (c,d) 1 wt% Au@Pd/C and (e,f) 1 wt% AuPd/ C samples dried overnight at 120 °C.

sintering with the median Pd@Au particle size increasing from 4.4 nm to 5.2 nm. In stark contrast, the sintering observed on carbon is much more pronounced with an identical heat treatment causing the Pd@Au median size to increase to more than 20 nm. This difference in sintering behaviour correlates directly with the differing extent in loss of catalytic activity observed on the two supports following calcinations at 400 °C (*i.e.* a factor of 2 for Pd@Au on TiO_2 and an order of magnitude for Pd@Au on carbon).

XPS results

Titania supported catalysts. Fig. 9 and 10 show the Au(4f) and Pd(3d) spectra for the series of titania supported Au–Pd catalysts. Also displayed on the Pd(3d) spectra are the Pd:Au molar ratios derived from the integrated XPS spectra. The Pd:Au molar ratio is as expected from the preparation methods, *i.e.* for the 1 wt% Au + Pd/TiO_2 catalyst is 1:1 and is close to 2:1 for all other samples. Calcination at 400 °C does not affect this ratio, in contrast to Au–Pd samples prepared by impregnation of titania where calcination results in a

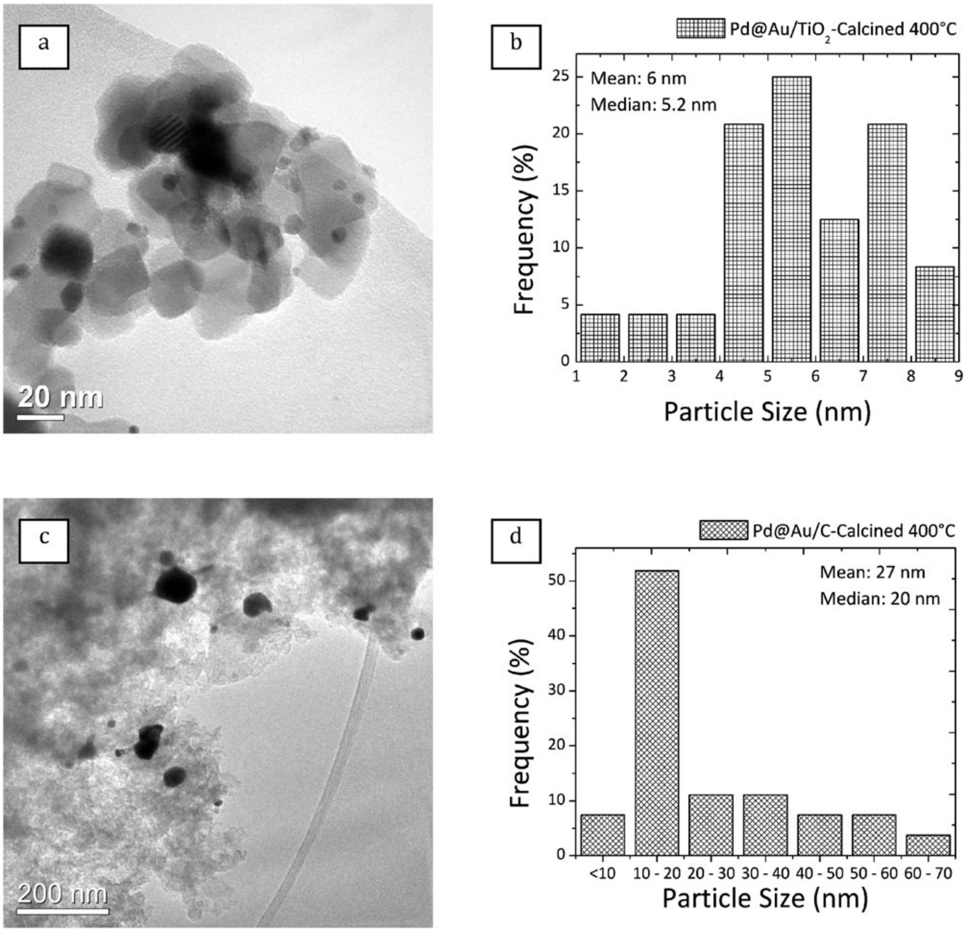

Fig. 8 Particle size distribution data, as determined from bright field TEM micrographs for (a,b) the 1 wt% Pd@Au/TiO_2 and (c,d) the 1 wt% Pd@Au/C calcined at 400 °C for 3 hours.

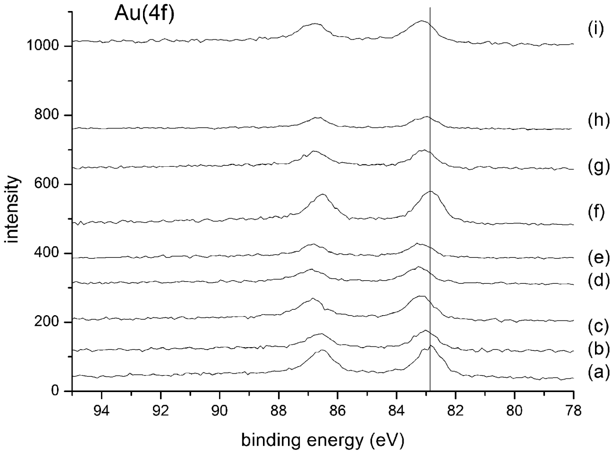

Fig. 9 Au(4f) spectra for the TiO_2 supported Au–Pd catalysts—AuPd: (a) dried and (b) calcined at 400 °C; Pd@Au: (c) dried, (d) calcined at 200 °C (e) calcined at 400 °C; Au@Pd: (f) dried, (g) calcined 400 °C; AuPd: (h) dried, (i) used for benzyl alcohol oxidation.

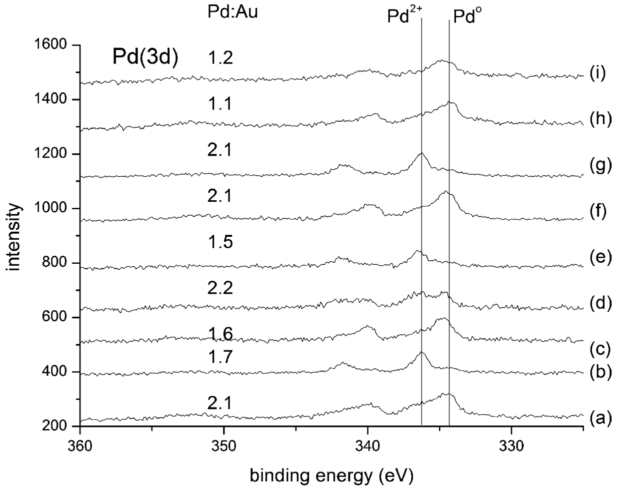

Fig. 10 Pd(3d) spectra for the TiO_2 supported Au–Pd catalysts—AuPd: (a) dried and (b) calcined at 400 °C; Pd@Au: (c) dried, (d) calcined at 200 °C (e) calcined at 400 °C; Au@Pd: (f) dried, (g) calcined 400 °C; AuPd: (h) dried, (i) used for benzyl alcohol oxidation. Pd:Au atom ratios are shown on the spectra.

significant increase in the Pd:Au ratio due to the formation of a Pd(shell)–Au(core) morphology.[22] The uncalcined catalysts contain Pd predominantly in the metallic state which transforms almost completely to Pd^{2+} after calcination at 400 °C.

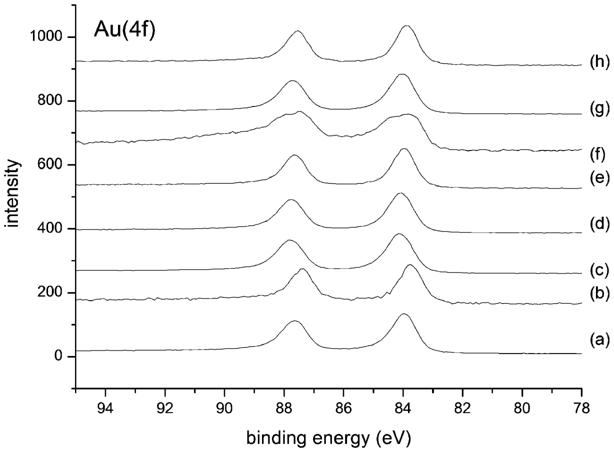

Fig. 11 Au(4f) spectra for the G60 supported Au–Pd catalysts—AuPd: (a) dried and (b) calcined at 400°C; Pd@Au: (c) dried, (d) calcined at 200 °C (e) calcined at 300 °C, (f) calcined at 400°C; Au@Pd: (g) dried, (h) calcined 400 °C.

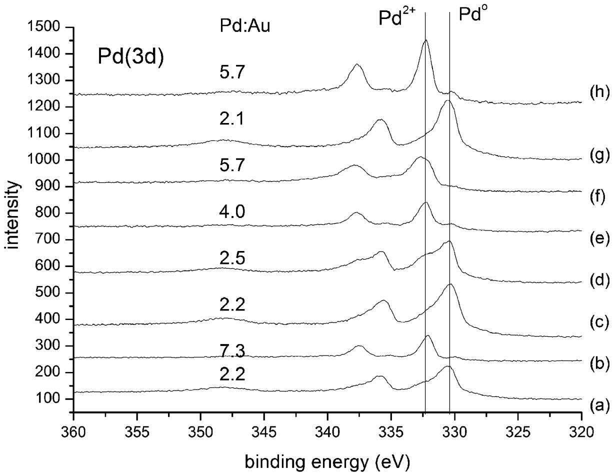

Fig. 12 Pd(3d) spectra for the G60 supported Au–Pd catalysts—AuPd: (a) dried and (b) calcined at 400 °C; Pd@Au: (c) dried, (d) calcined at 200 °C (e) calcined at 300 °C, (f) calcined at 400 °C; Au@Pd: (g) dried, (h) calcined 400 °C. Pd:Au atom ratios are shown on the spectra.

Carbon supported catalysts. Fig. 11 and 12 show the Au(4f) and Pd(3d) spectra for the series of carbon supported Au–Pd catalysts. Also displayed on the Pd(3d) spectra are the Pd:Au molar ratios derived from the integrated XPS spectra. In marked contrast to the titania-supported catalysts, we observe a significant increase in the Pd:Au molar ratio upon calcination. This is illustrated most clearly by the Pd@Au series of catalysts comprising the uncalcined, material, and samples calcined at 200 °C, 300 °C and 400 °C. The Pd:Au ratio increases monotonically from 2.2 to 5.7 and this is accompanied by the increasing oxidation of Pd^0 species to Pd^{2+}. Interestingly, both the Au@Pd and Pd@Au samples behave identically in this respect *i.e.* the order in which the metals are deposited is not important with regard to the Pd:Au ratio. The increasing Pd:Au ratio is consistent with the formation of core-shell particles[22] but we must also bear in mind the effect of particle size on detected XPS signal intensities, a high metal dispersion for a given amount of deposited metal resulting in a higher signal than for a lower dispersion.

Conclusions

The oxidation of benzyl alcohol under solvent-free conditions has been investigated using supported gold palladium bimetallic nanoparticles and comparing their activity and performance with mono-metallic catalysts. The catalysts prepared using the sol immobilisation technique show higher activity when compared with catalysts prepared by impregnation. In particular, much lower concentrations of the metals can be used and also the method can be tuned by preparing samples with gold or palladium seed sols. The Au–Pd catalysts were all more active than the corresponding monometallic supported Au or Pd catalysts. For the TiO_2-supported catalysts the order of metal addition (*i.e.* whether a gold seed sol or a palladium seed sol was used initially) in the preparation was not observed to be significant with respect to selectivity. For the carbon-supported catalyst the order of metal addition has a very marked affect on activity and the carbon-supported catalysts are also more significantly affected by heat treatment, *e.g.* calcination at 400 °C leads to the activity being decreased by an order of magnitude, whereas the TiO_2-supported catalysts show a 50% decrease in activity. The TEM analysis shows that the carbon-supported catalysts are much more sensitive to sintering and this is the cause of the lower activity observed. Toluene is observed as an unwanted by-product of the reaction and conditions have been identified that minimise its formation. It is proposed that toluene and benzaldehyde are formed by competing parallel reactions of the initial benzyl intermediate *via* an adsorbed benzylidene species that can either be hydrogenated or oxidised. In this way we identified reaction conditions that maximised the availability of oxygen on the catalyst surface and thereby favour the synthesis of benzaldehyde which is the required selective oxidation product.

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