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Reactivity studies of Au–Pd supported nanoparticles for catalytic applications

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ABSTRACT

The utilisation of gold–palladium nanoparticles either in the form of colloids or supported nanoparticles has received enormous attention in recent years. These materials are very effective for the transformation of organic compounds to highly useful chemical products. The catalytic materials are usually prepared using deposition–precipitation and impregnation techniques, but recently significant attention has been focused on the use of colloidal methods. Here we compare and contrast the preparation and catalytic reactivity of Au–Pd supported nanoparticles synthesised by deposition–precipitation and colloidal methods. The catalyst materials have been evaluated for three different reactions, namely, the oxidation of benzyl alcohol, the direct synthesis of hydrogen peroxide and the oxidation of carbon monoxide. In addition, we have focused our attention on the pre-treatment temperature and the improvement of the deposition–precipitation method by using urea and sodium borohydride for the preparation of highly active Au–Pd supported nanoparticles.

1. Introduction

The utilisation of gold and gold–palladium supported nanoparticles in the field of catalysis has grown enormously the recent years [1–4]. Typical reactions for the use of gold-based catalysts include the low temperature oxidation of CO [5–12], synthesis of vinyl chloride by the hydrochlorination of ethyne [13], the selective oxidation of alcohols [14–27], the selective oxidation of alkenes to epoxides [28,29] the synthesis of hydrogen peroxide [30–33] and selective hydrogenation [34]. In our previous papers we have shown that catalysts based on Au–Pd nanoparticles supported on a range of supports, *e.g.* carbon, titania, alumina and iron oxide can be effective catalysts for the oxidation of alcohols and polyols [35], as well as in the synthesis of hydrogen peroxide [33]. Moreover, we have emphasised that the alloying of gold with palladium leads to a significant enhancement in activity for alcohol oxidation and as well as in the hydrogen peroxide formation [33,35]. The principal method that had been used for the preparation of the metal-supported catalysts in the earlier publications has been the impregnation method. Recently, we have shown that the use of a sol-immobilisation method can also be very effective for the synthesis of Au and Au–Pd nanoparticles supported on carbon and titania, and the catalysts typically give very high productivity in the synthesis of hydrogen peroxide and in the oxidation of benzyl alcohol [36], glycerol [37,38], 1,2-propanediol [39] and the epoxidation of alkenes [40].

In this paper we report for the first time the hydrogen peroxide productivity of titania-supported catalysts synthesised by using the sol-immobilisation methodology and we focus on the metal loading and present the beneficial role of the addition of Pd to Au for these catalysts. In addition, we compare and contrast the reactivity of supported Au–Pd catalysts prepared using a deposition–precipitation method using urea as the precipitating agent in place of sodium hydroxide. We have also explored other preparation variables such as the effect of an acid pre-treatment on benzyl alcohol oxidation and the use of zeolites as support materials for the Au–Pd system for selective oxidation reactions.

2. Experimental

2.1. Materials

$HAuCl_4{\cdot}3H_2O$ (99.99% purity) and $PdCl_2$ (99.99% purity) were supplied by Johnson Matthey. Three supports were used namely titania (Degussa P25), activated carbon (Aldrich G60) and zeolite H-ZSM-5 (Zeolyst, Si:Al = 30). $NaBH_4$ of purity >96% (Aldrich), urea (99.0% purity) and polyvinylalcohol (PVA) (Aldrich, MW = 10,000, 80% hydrolyzed) were used in the preparation. Fresh stock aqueous solutions of $PdCl_2$ (Johnson Matthey) (acidified with HCl), $HAuCl_4{\cdot}3H_2O$ of the required concentration, $NaBH_4$ (0.1 M) and PVA (1%, w/w) were prepared.

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2.2. Catalyst preparation

A range of monometallic Au and Pd and bimetallic Au–Pd supported catalysts were prepared by the deposition precipitation method using urea. To produce a 2.5 wt% Au–2.5 wt% Pd/TiO_2 catalyst the detailed procedure was as follows: the support was added to an aqueous solution comprising $HAuCl_4$ and $PdCl_2$ (4.2×10^{-3} M) and urea (0.42 M). The initial pH was 2. The suspension, whose temperature was thermostatically held at 80 °C, was vigorously stirred for 4 h (during which time the pH increases and reaches 7.2). The material was then recovered by filtration, washed and dried. The catalyst was chemically reduced at room temperature, as follows: the required amount of the Au–Pd/TiO_2 catalyst was suspended in distilled water and then a freshly prepared solution of $NaBH_4$ (0.1 M) was added in the required proportion ($NaBH_4$/Au (mol/mol) = 5) with vigorous stirring at room temperature. The slurry was stirred for 30 min and after 2 h the slurry was filtered and the solid was washed thoroughly with distilled water (2 l of doubly distilled water). After filtration, a colourless filtrate indicated and verified by UV–vis spectra that all the metal particles were embedded onto the titania. The sample was dried at 120 °C overnight.

For the sol-immobilisation method the detailed procedure for the preparation of Au, Pd and Au–Pd supported catalysts have been described in detail elsewhere [36,38]. Briefly, for the synthesis of a Au–Pd/C catalyst synthesised by sol-immobilisation method the following procedure was used. To an aqueous fresh $PdCl_2$ 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. 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%. After 2 h the slurry was filtered, the catalyst washed thoroughly with distilled water (neutral mother liquors) and dried at 120 °C overnight.

The following notation is used for the catalyst samples used in this study: *I* denotes impregnation; *acid* denotes an acid pre-treatment of the support with nitric acid; *SI* denotes sol-immobilisation; *DPU* denotes deposition–precipitation using urea; *DPUC* denotes deposition precipitation using urea and reduction with sodium borohydride; *w* denotes Au and Pd are present in a 1:1 ratio by weight; and *m* denotes Au and Pd are combined in a 1:1 molar ratio.

2.3. Catalyst testing

2.3.1. Alcohol oxidation

Benzyl alcohol oxidation was carried out in a stirred autoclave 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 five 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. The reaction time was measured from the time that the mixture reached the reaction temperature and 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, an external calibration method was used.

2.3.2. Hydrogen peroxide synthesis

Catalyst testing was performed using a stainless steel autoclave (Parr Instruments) with a nominal volume of 50 ml and a maximum working pressure of 14 MPa. The autoclave was equipped with an overhead stirrer (0–2000 rpm) and provision for measurement of temperature and pressure. Typically, the autoclave was charged with the catalyst (0.01 g unless otherwise stated), solvent (5.6 g MeOH and 2.9 g H_2O), purged three times with CO_2 (3 MPa) and then filled with 5% H_2/CO_2 and 25% O_2/CO_2 to give a hydrogen to oxygen ratio of 1:2 at a total pressure of 3.7 MPa. Stirring (1200 rpm unless otherwise stated) was commenced on reaching the desired temperature (2 °C), and all experiments were carried out for 30 min unless otherwise stated. Gas analysis for H_2 and O_2 was performed by gas chromatography using a thermal conductivity detector and a CP – Carboplot P7 column (25 m, 0.53 mm id). H_2O_2 yield was determined by titration of aliquots of the final filtered solution with acidified $Ce(SO_4)_2$ (7×10^{-3} mol/l). $Ce(SO_4)_2$ solutions were standardised against $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ using ferroin as indicator.

2.3.3. CO oxidation

The catalytic activity for CO oxidation was determined in a fixed bed quartz microreactor, operated at atmospheric pressure. The feed consisted of $CO/O_2/N_2$ with a molar ratio of 0.5/19.9/79.6. The combined flow rate was maintained at 22.5 ml min^{-1}, and a constant catalyst loading of 50 mg was employed. The catalyst temperature was maintained at 25 °C by immersing the quartz bed in a thermostatically controlled water bath. Catalysts were tested for a minimum of 500 min, and analysis of the reaction product was carried out on-line using gas chromatography. Conversion was calculated on the basis of CO_2 concentration in the effluent, and carbon balances were 100 ± 2%.

2.4. Characterisation of catalysts

The materials prepared by impregnation and immobilisation have been extensively characterised in our previous studies using STEM-HAADF imaging and XPS [36,38,41]. We selected them for this comparative study because they are well characterised and can act as model systems. For completeness the relevant details concerning their structures are given here. Catalysts prepared with the impregnation method produce a broader particle size distribution and greater median size than the sol-immobilisation method. Specifically, catalysts synthesised by the impregnation method show that for both supports they comprise mainly small particles (*ca.* 2–10 nm). The AuPd/TiO_2 catalyst has particles mainly in the 2–5 nm range with *ca.* 8% of larger particles (>20 nm); whereas, the AuPd/C catalysts comprise particles mainly in the 3–8 nm range with *ca.* 20% larger particles (>20 nm). For the impregnated materials the supported Au–Pd alloys have been characterised extensively by STEM-XEDS [35,36,41] and have been shown to have contrasting morphologies. The TiO_2-supported material has a core–shell structure with a palladium-rich shell and a gold-rich core, an observation that is in common with other oxide-supported Au–Pd catalysts prepared by wet impregnation. In contrast the carbon-supported Au–Pd catalyst tends to contain homogeneous alloy particles. In addition, STEM-XEDS spectrum images showed that the composition of the metal nanoparticles varied with size, with the smallest particles being Pd-rich whereas the largest particles were highly Au-rich. The acid pre-treated Au–Pd/C catalysts (acid pre-treatment of the support) favoured the formation of a greater number of the smallest (Pd-rich alloy) particles at the expense of the intermediate and large particles [41].

We have previously reported the characterisation of catalysts prepared *via* the sol-immobilisation method [36,38,42]. The median diameter of the sol-immobilised pure-Au on both supports

Table 1
Liquid phase oxidation of benzyl alcohol for catalysts prepared by the sol-immobilisation method.[a].

Entry	Catalyst	Conv. (%)	Selectivity (%)[b]			Yield (%)[b]			TOF (h^{-1})[c]
			Toluene	Benzaldehyde	Benzoic acid	Toluene	Benzaldehyde	Benzoic acid	
1	1% Au/C_{SI}	5.2	9.4	72.6	2.2	0.5	3.8	0.1	2500
2	1% Au/TiO_{2SI}	4.3	4.8	86.3	1.6	0.2	3.7	0.1	2900
3	0.5% Au/TiO_{2SI}	2.7	5.0	83.3	2.1	0.1	2.3	0.1	4200
4	0.5% Au/C_{SI}	4.4	17.7	70.2	4.3	0.8	3.1	0.2	8800
5	1% Pd/C_{SI}	96.4	35.1	55.4	2.6	33.8	53.4	2.5	23,300
6	1% Pd/TiO_{2SI}	68.4	26.2	67.3	2.1	17.9	46.0	1.4	18,200
7	0.5% Pd/TiO_{2SI}	15.4	20.6	67.5	2.3	3.2	10.4	0.4	7900
8	0.5% Pd/C_{SI}	70.0	25.7	63.5	3.6	18.0	44.5	2.5	38,400
9	1% $(Au–Pd)/TiO_{2SIw}$	61.2	26.7	69.2	1.7	16.3	42.4	1.0	15,400
10	1% $(Au–Pd)/C_{SIw}$	81.1	40.9	55.0	1.3	33.2	44.6	1.1	35,400

[a] Reaction conditions: benzyl alcohol, 0.1 g of catalyst, $T = 120\,^{\circ}C$, time of reaction = 2 h, pO_2 = 150 psi, stirring rate 1500 rpm.
[b] Selectivity to toluene, benzaldehyhde and benzoic acid, benzylbenzoate present as by-product.
[c] Calculation of TOF (h^{-1}) after 0.5 h of reaction. TOF numbers were calculated on the basis of total loading of metals.

were about 4.0 nm, while for pure-Pd the median size on C was 5.0 nm, which was slightly greater than that for the TiO_2 support at 3.8 nm. The mean diameter and size spread of values for Pd particles on C were significantly larger than for the corresponding Au on C sample. The median particle sizes for the sol-immobilised AuPd alloy were 5.1 and 3.8 nm, respectively, on the C and TiO_2 supports. It is also important to note that the main advantage of the sol-immobilisation preparation method is that does not produce any of the large particle sizes that are commonly found in the catalysts prepared by impregnation. Therefore the particle size distribution is significantly narrower for the sol-immobilisation method as compared to those made by the impregnation method. STEM-HAADF images of typical alloy particles in the $AuPd/C_{SI}$ and $AuPd/TiO_{2SI}$ materials [38] show that the AuPd nanoparticles prepared by sol-immobilisation are homogeneous alloys.

3. Results and discussion

3.1. Benzyl alcohol oxidation

Monometallic Au, Pd and bimetallic Au–Pd catalysts, prepared using sol-immobilisation, impregnation and deposition–precipitation methods, were evaluated as catalysts for the oxidation of benzyl alcohol. Table 1 summarises the data for the oxidation of benzyl alcohol with the monometallic Au and Pd catalysts and the bimetallic (Au–Pd) catalysts synthesised using the sol-immobilisation method. In addition, the effect of the metal loading for the monometallic Au and Pd metals (0.5–1%) was also studied at the same reaction conditions (pO_2 = 150 psi, $T = 120\,^{\circ}C$, 1500 rpm stirrer speed and 100 mg of catalyst). As reported previously [42] under these particular experimental conditions diffusion limitations are avoided. It is clear from the initial turnover frequencies (TOF) in Table 1 that the bimetallic Au–Pd supported catalysts exhibit enhanced catalytic activity with respect to the monometallic Au catalysts. In fact, the 1 wt% (Au–Pd)/C catalysts give TOF's that are enhanced by a factor of 10–17 with respect to the 1 wt% Au/C material, which demonstrates the synergistic effect of adding Pd to Au [35]. However, with respect to the 1 wt% Pd/C sample, there is only a slight increase of the TOF by a factor of 1.4–2.0, which is in agreement with previous observations on supported catalysts synthesised by the impregnation method [43].

In the case of the 1 wt% (Au–Pd)/TiO_2 catalyst, the TOF value is enhanced by a factor of 7 with respect to the 1 wt% Au/TiO_2 material. For the 1 wt% (AuPd)/TiO_2 catalyst a very similar activity is observed as for the 1 wt% (Pd)/TiO_2 catalyst (Table 1), but the selectivity to benzaldehyde is improved by ~10% using the bimetallic system.

The effect of metal loading for the monometallic Au and Pd supported catalysts was also studied (Table 1). In the case of the Au/C catalysts, decreasing the Au loading from 1 to 0.5% leads to an increase of TOF by a factor 3.5, and the selectivity towards benzaldehyde is not significantly affected (Table 1, entries 1 and 4). The most important observation concerns the selectivity to toluene which is formed as a by-product in this reaction. There is a 2-fold increase of toluene formation on decreasing the Au loading. This trend suggests that increasing Au loading facilitates the benzaldehyde formation at the expense of toluene production.

In the case of the Pd/C catalysts, upon decreasing the Pd loading from 1 to 0.5%, there is an increase of TOF by a factor of 1.7, while the selectivity to benzaldehyde is increased up to 8% and the selectivity to toluene decreases by ~10% (Table 1, entries 5 and 8). To verify this trend the selectivity to toluene is reported at isoconversion (*e.g.* 70%) and we observe that for 1 wt% Pd/C and 0.5 wt% Pd/C the selectivity to toluene corresponds to 40 and 26%, respectively. Increasing the Pd loading also resulted in a significant increase in conversion with almost all of the initial benzyl alcohol being consumed. However, the change in selectivity seems to indicate that the increase in Pd loading facilitates toluene formation at the expense of benzaldehyde formation. It should be noted that Pd as a metal has a significant affinity for H abstraction from the alcohol to form a surface alkoxide species to give a surface Pd–H species, and that the oxidation of these Pd–H species is much slower than for Au–H species [44]. A possible consequence of the presence of surface hydrogen on the Pd nanoparticles on the reaction profile is that it could catalyse the formation of toluene through the hydrogenolysis of the C–O bond, as has been observed for Pd catalysts in liquid phase oxidation [45]. Thus, increasing the Pd loading leads to a higher concentration of Pd–H species (due to the high affinity of Pd for hydrogen adsorption) on the surface of the catalyst [46], and this leads to increased toluene formation.

For the Au/TiO_2 catalysts, a decrease of Au loading leads to an increase of TOF by a factor of 1.4, whereas selectivity to benzaldehyde does not vary (Table 1, entries 2 and 3). In addition, toluene formation is also not affected by the variation of the metal loading, which is in direct contrast to the behaviour the Au/C catalyst. This is probably related to different levels of conversion since the Au/C catalysts are far more active. However, these results emphasise the importance of the support in controlling the final distribution of products.

For the Pd/TiO_2 catalysts, a decrease in Pd loading decreases the TOF by a factor of 2.3 (Table 1, entries 6 and 7). This result is different to the case of Pd/C catalysts, since it retains a similar selectivity to benzaldehyde at isoconversion, again indicating the important role played by the support and we anticipate that this may be related to the dispersion of the Pd.

Comparison of the catalytic data between monometallic Au and Pd supported catalysts shows that Pd catalysts are by far more active than Au catalysts by a factor of 8–10 in terms of TOFs, whereas selectivity to benzaldehyde is much higher for the Au catalysts and toluene formation is significantly promoted by the Pd catalysts.

It is evident from the data presented in Table 1 that the most striking effect between the titania and carbon supports, is an increase of catalyst activity by a factor of almost 2 (based on TOF calculated after 30 min) when carbon is the chosen support for the immobilisation of the (Au–Pd) bimetallic-supported colloids (24,000–42,000 h^{-1} for carbon and 15,000–19,000 h^{-1} for titania). This increase in catalytic activity can not be explained on the basis of differences in particle size between the two materials since for both materials the mean particle size is very similar (4–5 nm). Other parameters, such as surface area, porosity and support chemical composition could be playing a role and especially considering the higher surface area of carbon (~1000 m^2/g) as compared to titania (~45 m^2/g) and the very different surface functionality. Another significant observation is the fact that when a carbon support is used the toluene formation is increased by a factor between 1.5 and 2 with respect to titania (23–26% selectivity to toluene using carbon and 38–44% selectivity to toluene using titania at similar conversion level), indicating the importance of the choice of support.

3.2. Comparison of impregnation versus sol-immobilisation preparation methods for benzyl alcohol oxidation

5 wt% (Au–Pd)/C catalysts were prepared by the impregnation method. Acid treatment in carbon-supported catalysts is known to improve dispersion of the supported metal [54,55], and we have recently shown that an specific pre-treatment of the carbon support with dilute nitric acid aids the dispersion of the Au–Pd metals deposited by impregnation and this reduces the mean particle size as well as improving selectivity in hydrogen peroxide synthesis [41]. In this study we have used both non-treated and acid pre-treated carbons and the final catalysts were calcined at 400 °C. These materials were tested for the liquid phase oxidation of benzyl alcohol using the same reaction conditions as employed previously. The treatment of the support with nitric acid adds some insight into possible correlations between toluene formation and the number density of acidic sites. A comparison can be made between the 1 wt% (Au–Pd)/C and 1 wt% (Au–Pd)/TiO_2 samples synthesised by the immobilisation method and calcined at the same temperature (400 °C). The catalytic data for these two materials are presented in Table 2. In terms of catalyst activity, as given by the TOFs values, the sol-immobilised 1 wt% (Au–Pd)/C catalysts are more active by a factor of 8–12 than the 5 wt% (Au–Pd)/C synthesised by the impregnation method. For the 1 wt% (Au–Pd)/TiO_2 catalyst the TOF is 10–18 times higher than that for the 5 wt% (Au–Pd)/C catalyst (Table 2, entries 1, 3 and 4). In terms of selectivity, the 1 wt% (Au–Pd)/C catalysts synthesised by the immobilisation method gives *ca.* 8–10% higher selectivity to benzaldehyde, 75–79% with the 1 wt% (Au–Pd)/C prepared by immobilisation and 62–69% with the 5 wt% (Au–Pd)/C prepared by the impregnation method. The acid pre-treated impregnated (Au–Pd)/C catalyst shows a similar level of activity, but higher selectivity towards toluene with respect to the untreated acid catalyst (Table 2, entries 4 and 5), suggesting that surface acidity could play a role in toluene formation.

3.3. Benzyl alcohol oxidation using supported Au–Pd bimetallic catalysts synthesised by deposition–precipitation

Au and (Au–Pd) catalysts supported on TiO_2 have also been prepared using a deposition precipitation method with urea as the precipitating agent adapted from the original work from Geus and van Dillen [49]. The choice of urea instead of sodium hydroxide affords depositing the total nominal loading of the metal onto the support while retaining small particle sizes (2–5 nm) [50–52]. Nevertheless a pre-treatment of the dried Au/TiO_2 and (Au–Pd)/TiO_2 materials following synthesis is necessary when urea is used, to enable the removal of the organic precursor residues deposited onto the support and the ligands on the metal nanoparticles. Hence, the pre-treatment of the synthesised material is performed at 120 and 400 °C in air to remove residual urea residues. In addition, our modified method employs *in situ* chemical reduction with $NaBH_4$ before the filtration of the slurry solution in order to generate small particles with a narrow distribution, without the need of a pre-treatment heating step [53]. For the deposition–precipitation synthesis of Au–Pd supported catalysts we have investigated two supports, namely zeolite (HZSM-5) and titania.

The catalytic data for the deposition precipitated materials are presented in Table 3. Comparison at the same heat pre-treatment temperature shows that H-ZSM5 can, in some instances be a superior catalyst support to titania. Increasing the heat pre-treatment temperature from 120 to 400 °C results in a significant decrease in catalyst activity for the zeolite-supported catalyst; whereas, for the titania-supported catalyst there is only a very slight enhancement in performance. We can attribute this difference in behaviour to the stronger metal-support interaction in a titania-supported catalyst as compared to the zeolite-supported catalyst, which probably inhibits nanoparticle sintering. Selectivity to benzaldehyde is in the range 80-90%, and benzyl benzoate and benzoic acid are the main by-products. Despite the pore structure and acidity of the H-ZSM-5, the product distribution is very similar for both catalysts and, considering its advantage in activity, H-ZSM5 should not be viewed as an inferior support but rather as an effective support for Au–Pd for certain selected catalytic applications. In addition, 1 wt% (Au–Pd)/TiO_{2DPUm} synthesised by deposition–precipitation was treated with $NaBH_4$, in order to (i) obviate the need for a heat pre-treatment step and (ii) enhance the formation of small Au–Pd nanoparticles having a narrow particle distribution. In these preparations the same metal/$NaBH_4$ molar ratio were utilised as used in the colloidal method. It has been demonstrated that for monometallic Au supported catalysts this $NaBH_4$ chemical treatment produces gold particles that are in the same range as generated by the colloidal method [53]. The result of this synthesis is very promising since high catalytic activity is obtained with the 1 wt% (Au–Pd)/TiO_{2DPUCm} material which is similar to that found for the 1 wt% (Au–Pd)/TiO_{2SIw} material (Table 3). In terms of the selectivity compared at isoconversion (Table 4, entry 5), significant formation of toluene is observed, as is the case of the bimetallic catalysts prepared by the colloidal method. These results suggest that similar catalytically active sites are generated with both of these preparation methods.

3.4. H_2O_2 synthesis and CO oxidation

3.4.1. Monometallic and bimetallic catalysts synthesised by the immobilisation method

Recently we have demonstrated that bimetallic Au–Pd supported nanoparticles on carbon prepared by sol-immobilisation are highly active for the synthesis of hydrogen peroxide [36]. In this paper we report for the first time the hydrogen peroxide activity of Au, Pd and bimetallic Au–Pd nanoparticles supported on titania by the sol-immobilisation method and compare their activity with the analogous catalysts supported on carbon. The catalytic data for these materials are presented in Table 5. Comparison between the monometallic Au, Pd and bimetallic Au–Pd supported catalysts indicates that the addition of Au to Pd markedly enhances the catalyst activity by factors of 36 and 27 for the carbon and titania-supported catalysts, respectively. In all the cases the Au–Pd supported nanoparticles are more active than the corresponding monometallic Au and Pd supported catalysts.

Monometallic Pd supported catalysts generate H_2O_2 at a higher rate than monometallic Au supported materials s with the rate

Table 2
Liquid phase oxidation of benzyl alcohol for catalysts prepared by the sol-immobilisation and impregnation methods and calcined at 400 °C in air.[a].

Entry	Catalyst	Conv. (%)	Selectivity (%)[b]			Yield (%)[b]			TOF (h^{-1})[c]
			Toluene	Benzaldehyde	Benzoic acid	Toluene	Benzaldehyde	Benzoic acid	
1	1% (Au–Pd)/TiO_{2SIw}	22.7	22.2	69.7	1.9	5.0	15.8	0.4	3900
2	1% (Au–Pd)/C_{SIw}	6.7	2.4	78.7	3.6	0.2	5.3	0.2	1800
3	5% (Au–Pd)/$C_{Iw\text{-}acid}$	2.4	15.7	67.2	0.0	0.4	1.6	0.0	350
4	5% (Au–Pd)/C_{Iw}	2.2	9.7	68.8	2.6	0.2	1.5	0.1	500

[a] Reaction conditions: benzyl alcohol, 0.1 g of catalyst, $T = 120\,°C$, time of reaction = 2 h, $pO_2 = 150$ psi, stirring rate 1500 rpm.
[b] Selectivity to toluene, benzaldehyhde and benzoic acid, benzylbenzoate present as by-product.
[c] 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
Benzyl alcohol oxidation performance after 6 h reaction with Au–Pd catalysts prepared by deposition precipitation methods: effect of support, treatment (calcination in static air) and chemical treatment (reduction with $NaBH_4$).[a].

Entry	Catalyst	Catalyst pre-treatment	Conv. (%)	Selectivity (%)				TOF (h^{-1})[b]
				Toluene	Benzaldehyde	Benzoic acid	Benzyl benzoate	
1	5% (Au–Pd)/TiO_{2DPUw}	Dried	7.2	0.6	83.2	6.6	9.6	1100
2	5% (Au–Pd)/TiO_{2DPUw}	Calcined 400 °C/air	8.6	1.1	91.9	2.8	4.2	1900
3	5% (Au–Pd)/$ZSM5_{DPUw}$	Dried	24.9	1.2	82.1	7.6	9.1	3200
4	5% (Au–Pd)/$ZSM5_{DPUw}$	Calcined 400 °C/air	15.6	2.0	81.6	6.1	10.3	1500
5	1% (Au–Pd)/TiO_{2DPUCm}	Dried	61.3	14.1	76.5	6.3	3.1	39,200

[a] Reaction conditions: benzyl alcohol, 0.05 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.

Table 4
Benzyl alcohol oxidation results at isoconversion for Au–Pd catalysts prepared by deposition precipitation methods: effect of support, calcination temperature and chemical reduction.[a].

Entry	Catalyst	Catalyst pre-treatment	Conv. (%)	Selectivity (%)			
				Toluene	Benzaldehyde	Benzoic acid	Benzyl benzoate
1	5% (Au–Pd)/TiO_{2DPUw}	Dried	7	0.6	83.3	6.5	9.6
2	5% (Au–Pd)/TiO_{2DPUw}	Calcined 400 °C/Air	7	0.9	90.0	3.0	6.1
3	5% (Au–Pd)/$ZSM5_{DPUw}$	Dried	7	0.4	88.0	3.5	8.1
4	5% (Au–Pd)/$ZSM5_{DPUw}$	Calcined 400 °C/Air	7	0.3	85.6	4.0	10.1
5	1% (Au–Pd)/TiO_{2DPUCm}	Dried	7	23.6	72.8	1.3	2.3

[a] Reaction conditions: benzyl alcohol, 0.05 g of catalyst, $T = 120\,°C$, $pO_2 = 150$ psi.

Table 5
Hydrogen peroxide productivity and benzyl alcohol conversion for catalysts prepared by the sol-immobilisation method.[a].

Entry	Catalyst	Hydrogen peroxide productivity (mol H_2O_2 kg_{cat}^{-1} h^{-1})	Hydrogen peroxide productivity (mol H_2O_2 mol_{metal}^{-1} h^{-1})
1	1% Au/TiO_{2SI}	1	17
2	1% Pd/TiO_{2SI}	13	139
3	1% (Au–Pd)/TiO_{2SIm}	41	585
4	1% Au/C_{SI}	0.2	4
5	1% Pd/C_{SI}	1.5	16
6	1% (Au–Pd)/C_{SIm}	54	820

[a] Reaction conditions: reaction time for H_2O_2 synthesis 30 min; mass of catalyst for H_2O_2 synthesis: 10 mg.
[b]Reaction conditions: benzyl alcohol, catalyst (0.1 g), $T = 120\,°C$, $pO_2 = 10$ bar, time of reaction = 6 h, stirring rate 1500 rpm. Calculation of TOF (h^{-1}) after 0.5 h of reaction. TOF numbers were calculated on the basis of total loading of metals.

of hydrogen peroxide formation being from 7 to 15 times higher. Depending on the support, the rates for hydrogen peroxide formation are increased by a factor of 4–9 when TiO_2 is used as the support instead of the active carbon.

The Au/TiO_2 and Au–Pd /TiO_2 catalysts prepared using the sol-immobilisation method were also tested for CO oxidation as shown in Figs. 1 and 2. For CO oxidation, the dried samples show very poor CO conversion, *i.e.* below 1% conversion. As in the case of the metal-supported catalysts prepared by deposition–precipitation, a pre-treatment method is necessary for these sol-immobilised materials. In order to activate the 1 wt% Au/TiO_2 it is essential to perform a heat pre-treatment procedure which removes the PVA stabilising ligands which can potentially block the active sites for CO oxidation [54–56]. We selected three different heat pre-treatments, which have previously been shown to significantly affect the activity and selectivity in benzyl alcohol oxidation for monometallic gold and palladium catalysts [25]. These heat pre-treatments are: (a) heat pre-treatment at 250 °C in air for 3 h, (b) heat pre-treatment at 250 °C in nitrogen for 3 h and (c) heat pre-treatment at 250 °C in hydrogen for 3 h. The highest catalyst activity is observed when the heat pre-treatment is performed under static air conditions, followed a pre-heat treatment in the presence of hydrogen and nitrogen. Time-on-line analysis shows that there is a progressive deactivation of the catalysts over the first 4 h when treated in the presence of air and nitrogen, after which the catalytic activity stabilizes at a steady value. It is note-

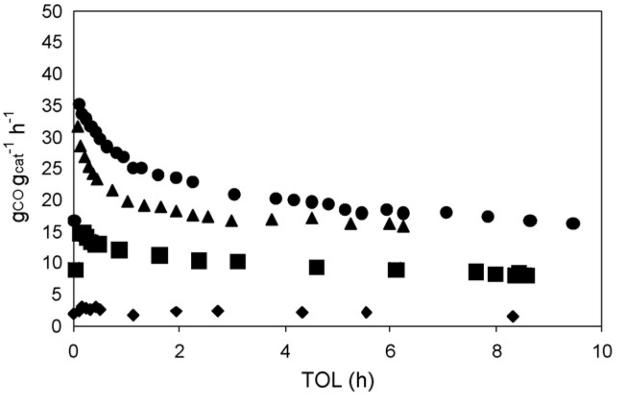

Fig. 1. Effect of heat pre-treatment temperature on CO oxidation using the 1 wt% Au/TiO_{2SI} catalyst: (a) key: ■ dried at 120 °C, (b) key: ● heat pre-treatment at 250 °C (static air conditions), (c) key: ▲ heat pre-treatment at 250 °C (flow using H_2) and (d) key: ♦ heat pre-treatment at 250 °C (flow using N_2).

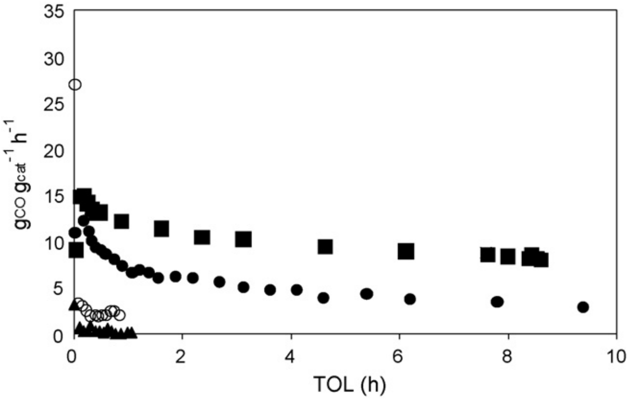

Fig. 2. CO oxidation using 1 wt% Au/TiO_{2SI}, 1 wt% Pd/TiO_{2SI} and 1 wt% $(Au–Pd)/TiO_{2SI}$ catalysts: (a) 1 wt% Au/TiO_{2SI} key: ■ dried at 120 °C, (b) 1 wt% Pd/TiO_{2SI} key: ▲ dried at 120 °C, (c) 1 wt% $(Au–Pd)/TiO_{2SI}$ key: ○ dried at 120 °C and (d) key: ● 1 wt% $(Au–Pd)/TiO_{2SI}$, calcination treatment at 400 °C.

worthy that the monometallic 1 wt% Au/TiO_2 is always more active than the bimetallic 1 wt% $Au–Pd)/TiO_2$, independent of the heat pre-treatment temperature used, indicating that the addition of palladium to gold by the sol-immobilisation method is not beneficial for improving CO oxidation performance. In addition, the 1 wt% Pd/TiO_2 sol-immobilised catalyst was found to be almost inactive.

3.4.2. Mono and bimetallic-supported nanoparticles synthesised by DP using urea

The effect of pre-treatment temperature was studied for the 5 wt% Au/TiO_2 and 2.5 wt% Au–2.5 wt% Pd/TiO_2 samples synthesised by the deposition precipitation method using urea instead of NaOH. Four different pre-treatment temperatures where tested, namely: 200, 400, 500 and 600 °C. The results of the hydrogen peroxide synthesis and CO oxidation experiments are presented in Fig. 3 for the monometallic 5 wt% Au/TiO_2 catalysts. The highest productivity and CO conversion was obtained for a pre-treatment temperature of 200 °C. Increasing the pre-treatment temperature beyond this leads to a progressive decrease in the CO conversion (98% at 200 °C to 60% at 600 °C) whereas the hydrogen peroxide productivity is decreased slightly at the heat pre-treatment temperature of 400 °C and progressively declines as the heat pre-treatment temperature is increased to 500 °C. Even higher heat pre-treatment temperatures do not affect the productivity of hydrogen peroxide, which is in stark contrast to the situation for CO conversion.

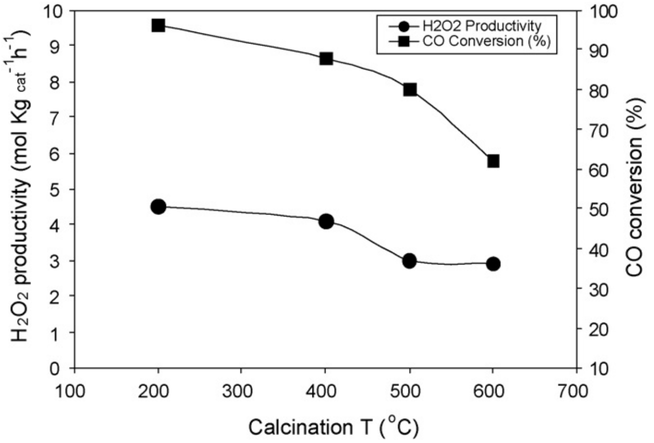

Fig. 3. Effect of calcination temperature on the catalytic performance of 5 wt% Au/TiO_{2DPU} (deposition–precipitation/urea): (a) key: ● H_2O_2 productivity and (b) key:■ CO conversion.

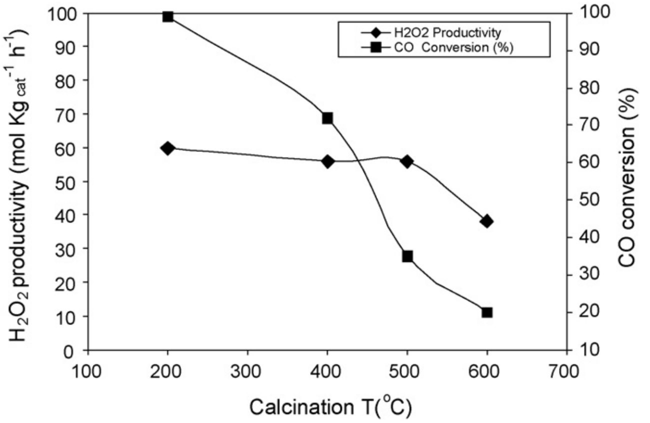

Fig. 4. Effect of calcination temperature 2.5 wt% Au–2.5 wt% Pd/TiO_{2DPU} (deposition–precipitation/urea): (a) key: ♦ H_2O_2 productivity and (b) key: ■ CO conversion.

In the case of the 2.5 wt% Au–2.5 wt% Pd/TiO_2 catalysts the variation of heat pre-treatment temperature results in a different productivity versus calcinations temperature profile in comparison to the monometallic 5 wt% Au/TiO_2 catalysts, as shown in Fig. 4. Increasing the heat pre-treatment temperature results in a significant decrease in the CO conversion, from 99% at 200 °C to 10% at 600 °C. In contrast, the level of productivity for hydrogen peroxide synthesis remains similar over the 200–500 °C. However, a significant 30% decrease is observed when the pre-treatment temperature is increased to 600 °C.

These observations indicate that the CO oxidation reaction is more sensitive than the hydrogen peroxide synthesis to the variation of gold particle size, which increases with increasing pre-treatment temperature. This relative insensitivity of the hydrogen peroxide reaction can be understood since both the synthesis and decomposition of hydrogen peroxide can be catalysed by the metal nanoparticles in the catalyst, and any particle growth sintering that occurs during heat treatment will affect the activity of the nanoparticles for both steps; *i.e.* particle growth could decrease the number of H_2O_2 molecules synthesised to some extent over the temperature range but simultaneously retain productivity by decreasing the number of sites responsible for the undesired H_2O_2 decomposition. This contrasts with the simplicity of CO oxidation, where it is well understood that very small gold nanoclusters can be active and that activity tends to decrease with increasing particle sizes >2 nm.

4. Conclusions

The oxidation of benzyl alcohol, hydrogen peroxide synthesis and oxidation of CO have been investigated using three methods for the synthesis of monometallic and bimetallic-supported nanoparticles (a) impregnation, (b) a colloidal sol-immobilisation method and (c) a deposition–precipitation method using urea. A strong synergistic effect is evident with the addition of Pd to Au, especially in the case in the synthesis of hydrogen peroxide. For bimetallic nanoparticles, titania is an inferior support to carbon for the oxidation of benzyl alcohol reaction and hydrogen peroxide synthesis. In addition, the sol-immobilised supported catalysts were tested for CO oxidation and it was observed that it is possible to activate the supported colloidal catalysts after a suitable thermal treatment to partially remove protective PVA ligands. For CO oxidation, the addition of palladium to gold is not beneficial in terms of catalyst activity. We also report the use a deposition–precipitation method using urea for the synthesis of gold and gold–palladium supported nanoparticles and show that by choosing an appropriate heat pre-treatment procedure it is possible to obtain very active catalysts for CO oxidation and as well as for hydrogen peroxide synthesis and benzyl alcohol oxidation. For this latter technique gold–palladium deposited on a zeolite H-ZSM5 support gave a catalyst that had the same product distribution but higher activities than their titania-supported analogues. Finally, the effect of heat treatment showed that CO oxidation is more sensitive to the precise heat treatment temperature than hydrogen peroxide synthesis, suggesting that the CO oxidation is a reaction that is significantly more sensitive to the particle size than the other reactions we have investigated.

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