The effect of catalyst preparation method on the performance of supported Au–Pd catalysts for the direct synthesis of hydrogen peroxide†

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The direct synthesis of hydrogen peroxide from H_2 and O_2 offers the possibility of a new green production method for this important commodity chemical. Active catalysts for this reaction are typically prepared using an impregnation method and it is important to identify improvements in the preparation methodology that can result in more active catalysts that retain their stability. The effect of the precise procedure by which the metals are impregnated onto TiO_2 and C supports during the preparation of supported Au–Pd catalysts has been investigated and it is shown that the two supports exhibit significant differences. The concentration of the solution of the mixed aqueous solution of $HAuCl_4$ and $PdCl_2$ immediately prior to the initial drying step has a profound effect on the structure and activity of the TiO_2-supported catalysts. TiO_2-supported catalysts prepared using impregnation with the minimal amount of added water whilst ensuring that the catalyst is not formed into a paste (*i.e.* still contains *ca.* 1.5–2 ml of H_2O) prior to drying at 110 °C exhibit very high activity (*ca.* 120 mol H_2O_2 kg_{cat}^{-1} h^{-1}) which is equivalent to the corresponding carbon-supported catalyst. The presence of more water (*ca.* 2–28 ml) in the catalyst impregnation step prior to drying leads to a significant change in the particle size distribution and a bimodal distribution is observed for the TiO_2-supported catalysts. These catalysts also show a change in the nature of the Au and Pd nanoparticles. Unfortunately, TiO_2-supported catalysts prepared in this manner are not stable on re-use. However, catalysts prepared using a similar method, but with the removal of *ca.* 75% of the initial H_2O ensuring that a paste is formed prior to drying, are found to be fully re-usable. In contrast, for carbon-supported catalysts dilution of the Au and Pd compounds during the initial impregnation step, coupled with subsequent removal of water to form paste with varying water content, did not affect the activity and these catalysts could be re-used without loss of catalyst performance. The effect of the catalyst structure on activity and re-usability is discussed.

Introduction

Hydrogen peroxide (H_2O_2) has found extensive use in the fine chemicals industry and for environmental protection as a benign oxidant. It is a major commodity chemical with a current annual usage of well over 2M tonnes per annum.[1] This is expected to increase significantly when production units for the synthesis of propene oxide come on stream. The current commercial process for the production of H_2O_2 is referred to as the indirect process and involves the sequential hydrogenation and oxidation of an alkyl anthraquinone, thereby avoiding the potential for explosive contact between hydrogen and oxygen to occur.[2] This process has been commercialised for over sixty years and has been extensively optimised to give high H_2 selectivities, which is a key feature governing the commercial viability of any process. The indirect process, however, has many non-green features. For example, the alkyl anthraquinone used in the indirect process degrades over time and this produces additional waste. However, the most important non-green feature is that the process is only economic on a large scale. Hence H_2O_2 is produced in a concentrated form and then is transported to the point of use where it has to be diluted as most applications require less concentrated solutions of H_2O_2. The initial concentration and subsequent dilution of the H_2O_2 incurs a very high energy utilisation cost. The introduction of a direct process would potentially overcome the requirement to produce concentrated solutions of H_2O_2 since it could be used at the point of production as a dilute solution.

The direct synthesis of H_2O_2 from molecular hydrogen and oxygen using metal-supported catalysts is considered to be an environmentally benign and economically attractive alternative to the indirect process.[1] It is a subject that has attracted considerable research attention, with until recently, most attention being

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focused on supported Pd catalysts.[3-21] Unfortunately, supported Pd catalysts suffer from a disadvantage that the catalysts are also active for the subsequent hydrogenation/decomposition of H_2O_2. To overcome this, halide and acid additives have to be used during the synthesis reaction,[18-21] and their subsequent removal and clean up poses serious non-green issues for the Pd-based catalytic route. We have shown, in recent studies,[22-32] that a combination of Pd with Au promotes both the activity and selectivity for the direct synthesis reaction. Most importantly the Au–Pd catalysts do not require the addition of halide and acid stabilisers during the synthesis reaction and hence these catalysts provide the basis for a green alternative to the current indirect process. For the direct catalysts to become competitive, it is essential that high activity Au–Pd catalysts are designed that retain high H_2 selectivity.

The role of the support has been recognised as an important catalyst design parameter. In previous studies we have shown that the nature of the support affects both the morphology of the Au–Pd nanoparticles as well as the particle size distribution.[27,31] TiO_2-supported catalysts have a core–shell morphology with a Au-rich core and a Pd-rich shell, whereas carbon-supported catalysts exhibit homogeneous Au–Pd alloys. There is a further difference as the carbon-supported catalysts tend to contain smaller Au–Pd nanoparticles.[31] Overall, the carbon-supported catalysts are more active and selective, typically displaying about twice the activity of the TiO_2-supported catalysts for H_2O_2 synthesis.[27] Active catalysts are prepared using an impregnation method and we have now investigated this process in more detail. A key aspect of green chemistry is the importance of exploring systematic variation for rational catalyst development, and this is the thrust of the research we now report. In particular we have focused on exploring the effect of catalyst preparation variables on the activity and stability of catalysts for the direct synthesis of H_2O_2 as this will be important in any attempt to implement this new green technology. In this way we have found that the concentration of the metal salts used for the impregnation can have a marked effect on the catalytic performance of the TiO_2-supported Au–Pd catalysts, but the carbon-supported catalysts are not affected by this parameter. However, by optimising the preparation parameters we have been able to produce TiO_2-supported catalysts that have the same activity as the high activity carbon-supported catalysts. In this paper we present this advance and discuss the origins of the effect.

Experimental

Catalyst preparation

Catalysts comprising 2.5 wt% Au/2.5 wt% Pd/support were prepared using the following standard method (all quantities stated are per gram of finished catalyst). $PdCl_2$ (0.042 g, Johnson Matthey) was added to a $HAuCl_4 \cdot 3H_2O$ solution (2.5 ml, 5 g in 250 ml) and stirred at 80 °C until the Pd dissolved completely. The appropriate support (0.95 g; TiO_2 (P25, Degussa, or Aldrich), or C (G60, Aldrich)) was then added to the solution and stirred to form a paste. The paste was dried (110 °C, 16 h) before calcination (400 °C, 3 h). This standard method was varied systematically by either adding water to the starting solutions, varying the stirring time at 80 °C prior to drying or by adding lower amounts of the support, thereby changing the consistency of the paste. The uptake of the Au and Pd compounds was monitored during the preparation procedure using UV-vis spectroscopy (V-570, JASCO) in H_2O between 200 and 800 nm, in a quartz cuvette. Samples (0.5 ml) were collected during the impregnation step at timed intervals after the support (C or TiO_2) was stirred with gold and palladium metal compounds in solution. Each sample was passed through glass filter paper (Whatman 55 micron grade) to carefully separate the solution from the support. Both concentrated (2 ml water) and dilute (28.5 ml water) metal solutions were studied to assess the effect of concentration on the rate of metal uptake.

Catalyst characterisation and testing

Hydrogen peroxide hydrogenation was evaluated using a Parr Instruments stainless steel autoclave with a nominal volume of 100 ml and a maximum working pressure of 14 MPa. To test each catalyst for H_2O_2 hydrogenation, the autoclave was charged with catalyst (0.01 g) and a solution containing 4 wt% H_2O_2 (5.6 g MeOH, 2.22 g H_2O and 0.68 g H_2O_2 (50%)). The charged autoclave was then purged three times with 5% H_2/CO_2 (0.7 MPa) before filling with 5% H_2/CO_2 to a pressure of 2.9 MPa at 20 °C. The temperature was allowed to decrease to 2 °C followed by stirring (at 1200 rpm) of the reaction mixture for 30 min. The above reaction parameters represent the optimum conditions we have established for the synthesis of H_2O_2.[26] The only difference is the absence of O_2 and the addition of H_2O_2 in the reaction mixture. The wt% of H_2O_2 hydrogenated was determined by titrating aliquots of the fresh solution and the solution after reaction with acidified $Ce(SO_4)_2$ (0.0288 M) in the presence of two drops of ferroin indicator.

Synthesis of H_2O_2 from H_2 and O_2 was performed using similar conditions in the presence of O_2 and with no added H_2O_2 (5% H_2/CO_2 and 25% O_2/CO_2, 1 : 2 H_2/O_2 at 4 MPa, 5.6 g MeOH, 2.9 g H_2O, 0.01 g catalyst and 1200 rpm). H_2O_2 productivity was determined by titration of the final filtered solution as described previously

XPS measurements were made on a Kratos Axis Ultra DLD spectrometer. Samples were mounted using double-sided adhesive tape, and binding energies referenced to the C(1 s) binding energy of adventitious carbon contamination taken to be 284.7 eV. Monochromatic AlK_α radiation was used for all analyses. The intensities of the Au(4f) and Pd(3d) features were used to derive Pd : Au surface molar ratios.

Samples were prepared for electron microscopy analysis by dispersing the powders in high-purity ethanol and allowing a drop of the solution to dry on a 300-mesh, Cu-supported lacey carbon film (SPI). Transmission electron microscopy (TEM) bright-field (BF) imaging and X-ray energy dispersive spectroscopy (XEDS) was carried out using a JEOL 2000FX TEM operating at 200 kV.

Results and discussion

Effect of catalyst preparation on the activity of TiO_2-supported catalysts for H_2O_2 synthesis

In our previous studies using TiO_2-supported Au–Pd catalysts we used a wet impregnation method where the support is added

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Table 1 Effect of the amount of water added during the impregnation step of catalyst preparation on the activity of TiO_2-supported catalysts for H_2O_2 synthesis (0.5 g preparation scale)[a]

H_2O/ml[a]	[Au]/mol l^{-1}[b]	[Pd]/mol dm^{-3}[b]	Productivity/mol H_2O_2/kg_{cat}/h[c]	Hydrogenation activity/mol H_2O_2/kg_{cat}/h[d]
2[e]	0.248	0.458	64	188
2	0.062	0.115	89	289
5	0.0105	0.0195	87	292
7	0.0079	0.0146	85	284
10	0.0058	0.0106	78	276
15	0.0042	0.0073	76	269
25	0.0024	0.0045	73	250
28.5	0.0021	0.0040	65	187
30	0.0020	0.0038	58	175

[a] 5 wt% AuPd/TiO_2 catalyst (0.5 g preparation scale) with water added during the impregnation step prior to drying (110 °C, 48 h). [b] Concentration of the metals prior to drying at 110 °C. [c] 30 min reaction. [d] 30 min hydrogenation of 4 mol% H_2O_2. [e] Catalyst formed into a paste by stirring at 80 °C to remove 75% of the 2 ml water present in the impregnation step.

to a concentrated solution of $HAuCl_4$ and $PdCl_2$ followed by stirring and gentle heating to form a very thick paste prior to drying in an oven at 110 °C.[26] This method typically led to a catalyst that, following calcination at 400 °C, was re-usable with a stable activity of *ca.* 64 mol H_2O_2 $kg_{cat}^{-1}h^{-1}$ measured using the standard reaction conditions at 0.5 h reaction time.[26] We have now investigated the effect of dilution of the metal salts and changes in H_2O content of the paste formed prior to drying during this impregnation method. The results for small scale preparation are shown in Table 1. The catalyst samples were all dried (110 °C, 48 h) and calcined (400 °C, 3 h) under identical conditions to the previously reported material.[26] It is apparent that as the concentration of the metal salts is increased, so does the activity of the final catalyst. Increasing the scale of the preparation using a higher mass of the support used also leads to an enhancement in the rate of formation of hydrogen peroxide (Table 2) and this further demonstrates the effect of the parameters of the concentration of the impregnating solution and the consistency of the paste that is formed prior to dying and calcination. Addition of water to the catalyst after the initial drying step (Table 3), *i.e.* re-wetting the catalyst, followed by re-drying prior to calcination does not have any significant effect on reactivity. This demonstrates the central importance of the drying step on the eventual catalyst performance. We have previously shown the critical influence of the calcination step with respect to catalyst stability, since calcination at temperatures below 400 °C leads to catalysts that leach Au and Pd during use.[26] However, it is now clear from this work that *all* heat treatment steps in the preparation of the supported Au–Pd nanoparticles are crucial.

Table 2 Effect of the amount of water added during the impregnation step of catalyst preparation on the activity of TiO_2-supported catalysts for H_2O_2 synthesis (1 g preparation scale)

H_2O/ml[a]	[Au]/mol dm^{-3}	[Pd]/mol dm^{-3}	Productivity/mol H_2O_2/kg_{cat}/h[b]
2	0.0619	0.115	117
5	0.0180	0.0333	117
7	0.0140	0.0260	115
10	0.0106	0.0195	115
15	0.0075	0.0138	112

[a] 5 wt% AuPd/TiO_2 catalyst (1.0 g preparation scale) with water added during the impregnation step prior to drying (110 °C, 48 h). [b] 30 min reaction.

Table 3 Effect of the addition of water after the impregnation step of catalyst preparation on the activity of TiO_2-supported catalysts for H_2O_2 synthesis

H_2O/ml[a]	Productivity/mol H_2O_2/kg_{cat}/h[b]	Productivity/mol H_2O_2/kg_{cat}/h[c]
2	95	120
5	94	120
7	94	119
10	93	120
15	92	121
20	92	
25	91	

[a] 5 wt% AuPd/TiO_2 catalyst; amount of water added after the impregnation and drying (16 h) prior to calcination. [b] H_2O_2 synthesis rate at 0.5 h for 0.5 g catalyst preparation scale. [c] H_2O_2 synthesis rate at 0.5 h for 1.0 g catalyst preparation scale.

It is apparent that by optimising the preparation conditions the activity of the TiO_2-supported catalysts can be affected by a factor of two, as the rate of H_2O_2 synthesis is increased from *ca.* 60 to 110–120 mol H_2O_2 kg_{cat}^{-1} h^{-1}. Increasing the drying time from 16 h up to 70 h led to a decrease in activity to *ca.* 80–90 mol H_2O_2 kg_{cat}^{-1} h^{-1}, further indicating the importance of the duration of the drying step.

We subsequently investigated the effect of the preparation conditions on the monometallic Pd catalyst and found that this gave the same high activity (100–105 mol H_2O_2 kg_{cat}^{-1} h^{-1}) if 2 ml of H_2O was used to dissolve the $PdCl_2$ and most of the water was not removed to form a thick paste prior to drying (Table 4). This indicates that the Au is not having a marked synergistic effect on the activity (increase from 105 mol H_2O_2 kg_{cat}^{-1} h^{-1} to 120 mol H_2O_2 kg_{cat}^{-1} h^{-1}) of the Pd catalyst when concentrated reagents are used during the impregnation step and most of the H_2O present is not removed to form a thick paste prior to drying. This is in marked contrast to the AuPd/TiO_2 catalysts prepared in a similar manner but with the formation of a thick paste during the impregnation step, which was the standard method we employed in all previous studies,[26] which demonstrate a marked synergistic effect on activity (increase from 31 mol H_2O_2 kg_{cat}^{-1} h^{-1} to 64 mol

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Table 4 Effect of the amount of water added during the impregnation step of catalyst preparation on the activity of TiO_2-supported 5% Pd/TiO_2 catalysts for H_2O_2 synthesis

Catalyst scale/g	H_2O[a]/mL	Productivity[b]/mol H_2O_2/kg_{cat}/h	Hydrogenation[c]/mol H_2O_2/kg_{cat}/h
1	2[d]	30	288
0.5	2	105	
1.0	2	100, 67[e]	239
1.0	5	79	329
1.0	10	68	234
1.0	28.5	23	178

[a] Amount of water added during the impregnation step prior to drying (110 °C, 16 h). [b] H_2O_2 synthesis rate at 0.5 h. [c] H_2O_2 synthesis rate at 0.5 h. [d] Catalyst formed into a paste by drying at 80 °C to remove 75% of the 2 ml water present in the impregnation step. [e] H_2O_2 productivity for 2nd use.

H_2O_2 kg_{cat}^{-1} h^{-1}) when Au is added to Pd. In retrospect we conclude that the underlying reason for this effect is that in the previous studies we removed 75% of the water present in the impregnation step prior to drying. In this way we formed a thick paste prior to drying and we consider this step crucial to obtain catalysts that demonstrate a marked synergistic effect on addition of gold to palladium.[26] However, these catalysts show a lower activity (64 mol H_2O_2 kg_{cat}^{-1} h^{-1}) when compared with catalysts that are not made into a paste before drying (Table 1). The role of Au in enhancing H_2O_2 formation is mainly related to its ability to limit the subsequent hydrogenation/decomposition of H_2O_2 formed. It will be shown later that the effectiveness of Au in doing this depends on its alloying with Pd and the formation of small alloyed nanoparticles.

Effect of catalyst preparation on the activity of TiO_2-supported catalysts for H_2O_2 hydrogenation and decomposition

The effect of the dilution of the Au and Pd precursors during the impregnation step was investigated for the effect on the hydrogenation of H_2O_2. In these experiments an initial solution of 4 mol% H_2O_2 was reacted in the presence of H_2 but in the absence of O_2 so that the hydrogenation activity of the catalyst could be determined. The results, shown in Table 1, show a similar trend to that observed in the synthesis of H_2O_2, since as the amount of water added in the impregnation stage is decreased the hydrogenation activity is markedly increased for low amounts of additional water. In addition, experiments for H_2O_2 decomposition in the presence of O_2 but in the absence of H_2 show that the decomposition activity is similarly enhanced (see ESI†). These results show that the main effect by which the rate of H_2O_2 synthesis is enhanced by using more concentrated reagents during the impregnation step of the preparation originates from an enhanced hydrogenation activity of the catalyst for both H_2O_2 synthesis and its sequential hydrogenation.

Effect of catalyst preparation on the activity of carbon-supported catalysts for H_2O_2 synthesis

The effect of dilution of the precursor salts and the drying time on the activity of carbon-supported Au–Pd catalysts was investigated, but these changes in conditions did not lead to any significant changes in activity (Table 5). Clearly there are significant differences between the carbon- and the TiO_2-supported catalysts. One key aspect is textural. When the precursor solutions are added to the TiO_2 a homogeneous suspension is formed for all amounts of the water dilution (see ESI†). This was not the case for the carbon support, which rapidly separates from the added solution (see ESI†). Furthermore, the adsorption of the Au and Pd onto the carbon is extremely rapid with adsorption of the Au and Pd compounds in the impregnation solution occurring immediately, and this limits the possibility for this preparation parameter to affect significantly the outcome of the preparative procedure with the carbon support. This is not the case for TiO_2-supported catalysts where the adsorption of Au and Pd is observed to be very slow even after taking into account the difference in surface area of the TiO_2 as compared to the carbon support (see ESI†).

Table 5 Effect of the amount of water added during the impregnation step of catalyst preparation on the activity of carbon-supported catalysts for H_2O_2 synthesis

H_2O/ml[a]	[Au]/mol dm^{-3}	[Pd]/mol dm^{-3}	Productivity/mol H_2O_2/kg_{cat}/h[b]
2 (16 h drying)	0.0619	0.115	120
2 (48 h drying)	0.0619	0.115	120
28.5 (48 h drying)	0.0041	0.0077	124

[a] 5 wt% AuPd/carbon catalyst (1.0 g preparation scale) with water added during the impregnation step prior to drying. [b] 30 min synthesis.

Catalyst re-usability

The re-usability of the catalysts was investigated. The carbon-supported catalysts were found to be fully reusable as has been previously noted.[27] This was observed regardless of the degree of dilution of the Au and Pd compounds. In contrast, the high activity TiO_2-supported catalysts could not be re-used with retention of the high activity (Table 6). In addition, even catalyst prepared using the addition of water showed instability since it steadily lost activity on use. For TiO_2 catalysts we have previously shown[26] that catalysts with stable activity can be prepared if no additional water is added to the preparation at the impregnation stage, and that as an additional step 75% of the water present in the impregnation step is removed by slow evaporation at 80 °C prior to the drying step. There are clearly marked differences between the carbon- and TiO_2- supported catalysts. We consider this to be related to the fundamentally different manner in which the Au and Pd compounds are adsorbed onto the support during impregnation. For the carbon support this process is facile,

Table 6 Reuse of $AuPd/TiO_2$ catalysts

	Productivity/mol H_2O_2/kg_{cat}/h[b]		
H_2O/ml[a]	1st use	2nd use	3rd use
2[b]	64	62	62
2	95	30	21
28.5	64	54	44

[a] Amount of water added during the impregnation step. [b] Catalyst formed into a paste by drying at 25 °C by removing 75% of the water present in the impregnation step.

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whereas for titania lower amounts are adsorbed and variations in the preparation parameters can have a marked effect on the stability and activity of the catalyst.

Characterisation of the catalysts

It is apparent that changing the solution concentration of the metal compounds during impregnation or varying the H_2O content in the paste formed prior to drying has a profound effect on the activity for the TiO_2-supported catalysts, as these show enhanced activity but with a decreased synergistic effect for the addition of Au to Pd. In contrast the carbon-supported catalysts are not affected and show the activity, marked synergy and reusability that we have reported previously.[27] To gain an understanding of the origins of this effect we have characterised the TiO_2-supported catalysts using XPS, transmission electron microscopy and UV-visible spectroscopy.

We have analysed selected catalyst samples using XPS in order to study any surface compositional changes that may be induced by the water treatment. Table 7 summarises the quantified XPS data, and in particular the Cl/Ti and Pd/Ti surface atom ratios for a series of Au–Pd/TiO_2 catalysts treated during the impregnation procedure with additional volumes of water in the range 0–28.5 ml. The addition of water clearly leads to a significant decrease in surface Cl concentration levels, even for the 7 ml treatment. After the addition of 28.5 ml of water during the impregnation step the surface Cl concentration is *ca.* 20% of that observed for the undiluted catalyst. For all of the samples the Pd(3d) spectrum shows the presence of both Pd^{2+} and Pd^0 species, with Pd^{2+} being dominant (Fig. 1). A curve fitting analysis of these spectra allows us to quantify the Pd^{2+}/Pd^0 ratio which is plotted as a function of water volume added in Fig. 2. The treatment with additional water also clearly leads to a relative increase in the metallic Pd content, which may reflect preferential leaching of Pd^{2+} species or that smaller Pd particles are inherently higher in Pd^0.

Bright field TEM micrographs of a sub-set of the AuPd on TiO_2 samples are presented in Fig. 3. All the samples showed a bimodal distribution of metal nanoparticles such as that shown in Fig. 3(a). The larger particles, which were in the 20-80 nm size range, were found by X-ray energy dispersive spectroscopy (XEDS) point analyses to contain Au. In contrast, the smaller particles which ranged between 2 and 10 nm in size, were found by XEDS to be Pd. To the detectability limit of the XEDS technique in this particular microscope (~1 at%), no strong alloying of the Au or Pd were found in either the smaller or larger types of metallic particle. Representative higher magnification views of the smaller particles for the 2 ml H_2O treated, 10 ml H_2O treated, and 28.5 ml H_2O treated samples are shown in Fig. 3(b), 3(c) and 3(d), respectively. While the population of

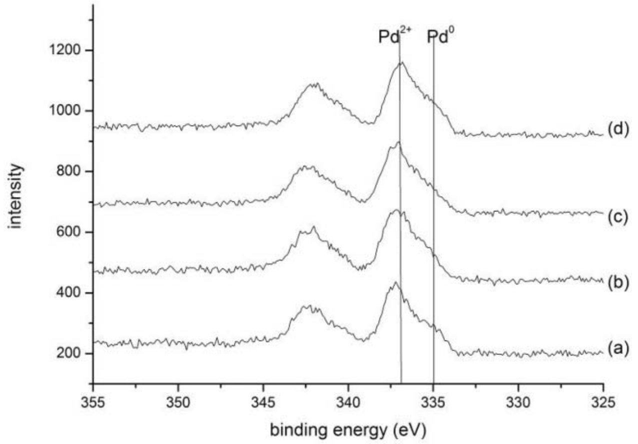

Fig. 1 Pd(3d) photoemission spectra for the Au–Pd/TiO_2 catalysts after (a) 2 ml, (b) 7 ml, (c) 15 ml, (d) 28.5 ml addition of water during the impregnation procedure, showing the presence of both oxidised and metallic Pd species.

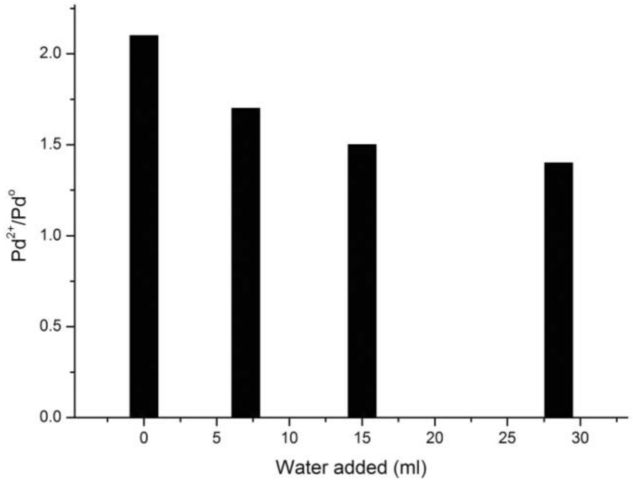

Fig. 2 Variation of the Pd^{2+}/Pd^0 ratio for Au–Pd/TiO_2 catalysts with the volume of water added during the impregnation procedure.

Table 7 Summary of quantified XPS data for the AuPd/TiO_2 catalysts

		Composition atom (%)			Atom ratios			
Drying time/h	Water added/ml	Au	Pd	Cl	Au/Ti	Pd/Ti	Cl/Ti	Pd/Au[a]
16	2	0.150	1.90	1.75	0.0052	0.066	0.061	12.1
16	7	0.068	1.13	1.19	0.0023	0.039	0.041	16.1
16	15	0.079	1.04	0.89	0.0029	0.038	0.033	12.6
48	2	0.065	1.44	2.00	0.0023	0.051	0.071	21.6
48	7	0.079	1.18	0.74	0.0027	0.041	0.026	14.4
48	10	0.110	1.20	0.89	0.0038	0.041	0.031	10.3
48	15	0.059	1.18	0.77	0.0021	0.042	0.028	19.4
48	28.5	0.047	0.82	0.44	0.0017	0.030	0.016	16.9

[a] Corrected for peak overlap.

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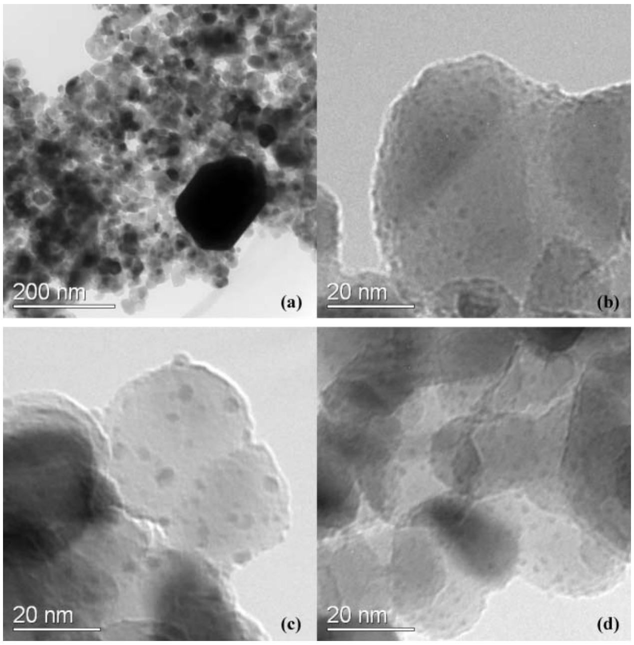

Fig. 3 Typical bright field TEM images from the AuPd/TiO_2 samples which were treated with (a,b) 2 ml, (c) 10 ml and (d) 28.5 ml of water.

larger, Au particles showed negligible differences in their size distribution, the smaller Pd particles showed a definite shift to a smaller median particle size for the samples treated with 10 ml and 28.5 ml of water (Fig. 4).

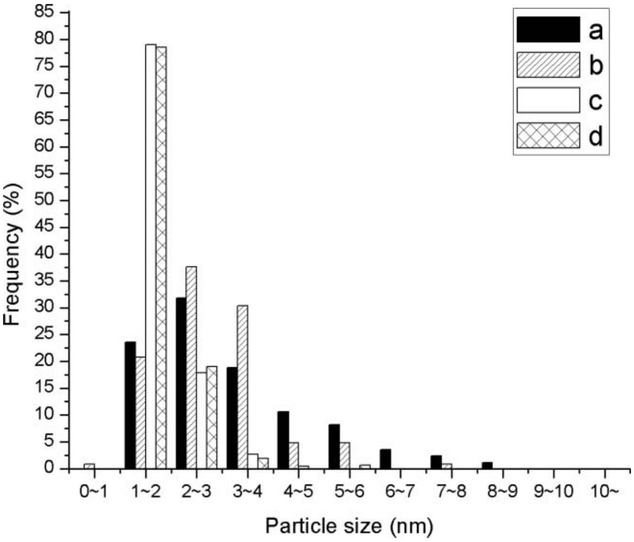

Fig. 4 Comparison of the size distributions for the smaller Pd-particles only found in the AuPd/TiO_2 samples. Key: (a) solid black – 2 ml, water added; 75% H_2O removed to give paste, (b) single line – treated with 2 ml water, (c) solid white – treated with 10 ml water, (d) cross hatch – treated with 28.5 ml water.

We have previously published[27,33,34] some very detailed electron microscopy characterisation results from AuPd/TiO_2 catalysts prepared using a similar method, but with the removal of *ca.* 75% of the initial H_2O (*i.e.* standard 'paste' samples). These studies revealed a bi-modal particle size distribution in which the smallest particles fell in the 1 nm to 8 nm size range, and a long tail of larger particles existed in the 20–200 nm size range. X-Ray energy dispersive spectroscopy (STEM-XEDS) spectrum images also showed all the metal nanoparticles particles were AuPd alloys, but that their composition varied with size in a systematic manner,[27,33,34] such that the smallest particles tended to be Pd-rich while the largest particles were highly Au-rich. The STEM-XEDS data also conclusively demonstrated that the larger alloy nanoparticles had Pd-rich shells and Au-rich cores. For comparative purposes with the AuPd/TiO_2 water treated samples, the particles at the lower end of the size distribution for this previously examined 'paste' sample are also included in the particle size histogram shown in Fig. 4. The essential difference for the population of smaller particles in the standard 'paste' sample was that even though their average particle size was slightly larger, they had a detectable and significantly higher Au content (~2 at%) within the Pd particles.

In comparison, Fig. 5(a) and 5(b) show two representative TEM images of the AuPd/activated C sample treated with 2 ml and 28.5 ml of H_2O, respectively. Both of these samples exhibited a very definite bimodal size distribution of particles. The very largest particles (not shown) were 20–100 nm in size and apparently contained only Au. If any Pd were present at all in these large particles, it was below the detectability

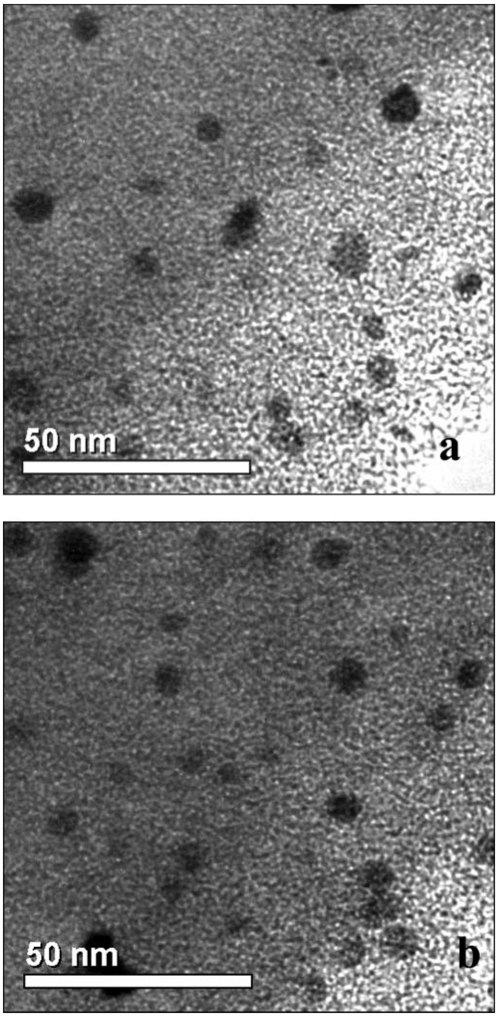

Fig. 5 Typical bright field TEM images from the AuPd/C samples which were treated with (a) 2 ml, and (b) 28.5 ml of water.

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limit of our XEDS technique. The smaller (3–10 nm) particles on the other hand only exhibited characteristic Pd XEDS peaks Furthermore, no significant difference in the particle size distribution of either the small or large particles was found between the samples treated with 2 and 28.5 ml of water, which is consistent with the invariant nature of the catalytic performance of these two samples.

In summary, Au–Pd/TiO_2 catalysts prepared using the impregnation method in which the catalyst is reduced to a thick paste prior to drying show a bimodal distribution of Au and Pd nanoparticles (small particles 1–8 nm and larger particles 20–200 nm) with the larger particles having a core–shell morphology comprising a Au-rich core and Pd-rich surface. The smaller particles were all AuPd alloys, with a very high Pd fraction, but still detectable Au content. The presence of these small Au–Pd alloy nanoparticles on the catalytic surface accounts for the lower H_2O_2 hydrogenation/decomposition activity over this catalyst and this explains the observed marked synergistic effect. Contrarily, Au–Pd/TiO_2 catalysts prepared using the new methodology (in which 2–28 ml of H_2O is present in the catalyst prior to drying) show a bimodal distribution of Au and Pd nanoparticles with larger particles (20–80 nm) containing Au and small particles (1–10 nm) containing Pd; no detectable Au–Pd alloy formation was found in either the smaller or larger particles. We consider these larger Au particles to be ineffective in limiting H_2O_2 hydrogenation/decomposition and as a result a reduced synergistic effect of Au is observed. The higher H_2O_2 formation and hydrogenation activity of the Au–Pd and Pd-only catalysts prepared using the new methodology is, therefore, solely related to the enhanced Pd dispersion.

Conclusions

We have shown that the manner in which the co-impregnation of Au and Pd onto a TiO_2 support is carried out profoundly affects the structure and activity of the final catalyst. In particular, the decrease in concentration of the metal compounds leads to a bimodal distribution of metal particles in the dried and calcined catalyst. The small metal particles comprise Pd only, within the limits of XEDS detection, whereas the large particles comprise almost entirely Au. The non-alloyed catalyst does not exhibit the marked synergistic effects on the catalyst performance usually observed for the addition of Au to Pd. The increase in activity that is observed for the TiO_2-supported Pd and Au–Pd catalysts is considered to be due to enhanced dispersion of the Pd and much smaller, more active, particles are synthesised. This leads to an enhancement in the hydrogenation activity of the catalyst. However, the enhancement in rate is a temporary phenomenon and the catalysts are not stable on reuse. In contrast, the preparation of the AuPd/TiO_2 catalyst with concentrated Au and Pd compounds in the initial impregnation step and the removal of most of the H_2O present to form a thick paste prior to drying leads to a lower activity catalyst, but this can be reused and does exhibit a marked synergistic effect on addition of Au to the Pd, as we have shown in detailed previous studies.[26] This marked synergistic effect can be attributed to the presence of smaller Au–Pd alloy nanoparticles in this catalyst. Dilution of Au and Pd precursors during the impregnation step or the change in the H_2O content of the paste prior to drying has no effect on the subsequent activity of the carbon supported catalysts and we consider this to be due to the rapid adsorption of the Au and Pd compounds onto activated carbon and this facilitates subsequent alloy formation. Hence by using a rational approach for the preparation of catalysts we have designed a preparation methodology that produces high activity catalysts which maximise the interaction between the Au and Pd but also ensuring that the nanoparticles produced remain stable which is a central tenet of green chemistry.

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