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Oxidation of benzyl alcohol using supported gold–palladium nanoparticles

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ABSTRACT

A key discovery in the last two decades has been the realisation that gold, when prepared as supported nanoparticles, is exceptionally effective as an oxidation catalyst, particularly for the oxidation of alcohols. The catalytic efficacy is enhanced further by the alloying of gold with palladium. In this paper we study the effect of the method preparation of gold–palladium alloy nanoparticles supported on titania and investigate the activity of the materials for the selective oxidation of benzyl alcohol. We contrast impregnation and deposition–precipitation methods and demonstrate that the most active catalysts are prepared using the deposition–precipitation method.

1. Introduction

The oxidation of alcohols using gold catalysts has become a research topic of great interest. Indeed, the field of gold catalysis continues to attract great interest. Until about 20 years ago, the chemistry of gold was dominated by the perception that gold was non-reactive since in its bulk state it is the most noble of the elements. Indeed, at moderately elevated temperatures the metal form is preferred and since bulk gold metal does not chemisorb oxygen it was perhaps realistic to consider that gold would not be an effective oxidation catalyst. However, two discoveries in the 1980s [1] that gold could not be just an outstanding catalyst but could be the best catalyst for two reactions, namely the oxidation of carbon monoxide [2,3] and the hydrochlorination of ethyne [4–8]. This has led to an explosion of interest in catalysis by gold [9–19]. Gold catalysts have now been found to be very active as catalysts for the epoxidation of alkenes [20,21], the oxidation of alcohols [22] and demanding hydrogenation reactions [23].

The oxidation of alcohols is of immense importance in the fine chemicals industry, and in particular the oxidation of primary alcohols to aldehydes is an important process for the synthesis of these highly valuable intermediates [24]. Even today oxidations of this type are carried out at a commercial scale using stoichiometric oxygen donors such as chromate or permanganate, but current environmental concerns are forcing the replacement of these routes. With the recent advent of green chemistry and its application industrially there is a need to identify atom-efficient oxidation reactions that can be carried out with molecular oxygen, rather than an activated form of oxygen, using mild solvent-free reaction conditions. In this respect the oxidation of alcohols to aldehydes represents a demanding target. Rossi et al. [25–27] in their seminal studies were the first to clearly demonstrate that supported gold nanoparticles can be very effective catalysts for the oxidation of alcohols. A key observation was that diols are oxidised to the corresponding mono-acids by oxidation of the primary alcohol group rather than the secondary alcohol, which might have been expected to be more reactive. The presence of base (typically NaOH) was found to be essential for activity and consequently sodium salts of the acids were formed as products. Recently Corma and co-workers [22,28–30] have shown that an Au/CeO_2 catalyst is active for the selective oxidation of alcohols to aldehydes and ketones and the oxidation of aldehydes to acids in the absence of base and under solvent-free conditions. Subsequently, we showed that the combination of Au and Pd as alloy nanoparticles significantly enhanced the catalytic activity for the oxidation of alcohols and the synthesis of hydrogen peroxide [31,32]. In this paper we now undertake an investigation of two methods of preparation for the AuPd/TiO_2 catalyst and investigate their use for benzyl alcohol oxidation.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of AuPd/TiO_2 by wet impregnation

Catalysts were prepared supported on titania (P25 Degussa), using a wet impregnation technique. 2.5 wt.% Au–2.5 wt% Pd/support was prepared by impregnation of the support using

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Table 1
Conversion of benzyl alcohol and turnover frequencies (TOF) after 0.5 h reaction.[a]

Temperature (°C)	Conversion at 0.5 h (%)	TOF at 0.5 h (h^{-1})
100	0.19	26
120	1.5	1300
140	4.3	3690
160	33.2	28400

[a] Reaction of 2.5% Au + 2.5% Pd/TiO_{2IMP} (25 mg) at various temperatures with 10 bar O_2 and stirred at 1500 rpm.

aqueous solutions of palladium chloride (Johnson Matthey) and $HAuCl_4 \cdot 3H_2O$ (Johnson Matthey). The detailed procedure for the preparation of 2 g of the 2.5 wt.% Au–2.5 wt% Pd/support catalyst is as follows: palladium chloride (83.3 mg) was dissolved in a stirred and heated aqueous solution (5 ml) of $HAuCl_4$ (5 g in 250 ml water). The resultant solution was then added to the titania support (1.9 g) and the resulting slurry was dried at 80 °C for 16 h. The resulting powder was ground and calcined in static air (400 °C, 3 h). This material was designated 2.5% Au + 2.5% Pd/TiO_{2IMP}.

2.1.2. Preparation of AuPd/TiO_2 by deposition–precipitation

A stirred, heated (60 °C) slurry of titania (1.9 g, Degussa, P25) in water (300 ml) was adjusted to pH 8 by the dropwise addition of (1 M) sodium carbonate. Palladium nitrate (119 mg) was dissolved in a stirred and heated aqueous solution (5 ml) of $HAuCl_4$ (5 g in 250 ml water solution) and this solution was added dropwise to the slurry with the simultaneous addition of sodium carbonate solution to maintain the overall pH at 8. After all the gold–palladium solution had been added the slurry was maintained at pH 8 for 1.5 h. The slurry was then filtered, washed with deionized water (1 l). The washed solid was dried (80 °C for 16 h) and calcined in static air (400 °C for 3 h). This material was designated 2.5% Au + 2.5% Pd/TiO_{2DP}. A variation in the deposition–precipitation procedure was investigated in which rather than setting the pH at 8.0 throughout the preparation, the pH was gradually raised to pH 8.0 during the precipitation procedure (all other preparation conditions remained the same). This material was denoted 2.5% Au + 2.5% Pd/TiO_{2DP2}.

2.2. Catalyst characterization

The catalyst was characterized using X-ray photoelectron spectra (XPS). XPS were recorded on a Kratos Axis Ultra DLD spectrometer employing a monochromatic Al Kα 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.

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.

2.3. Benzyl alcohol oxidation

The benzyl alcohol oxidation reactions were carried out in a stirred reactor (100 ml, Autoclave Engineers Inline MagneDrive III). 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 standard samples. For the quantification of the amounts of reactants consumed and products generated, the external calibration method was used.

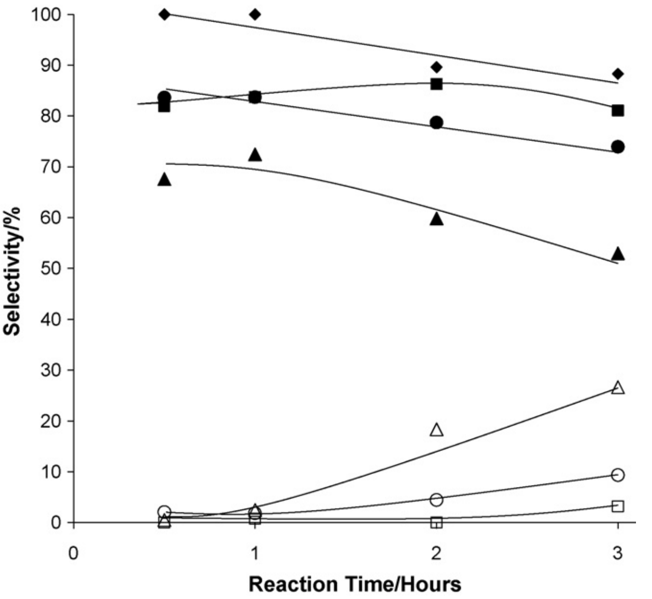

Fig. 1. The selectivity towards benzaldehyde (closed symbols) and benzoic acid (open symbols). Key: 100 °C (♦), 120 °C (■), 140 °C (●) and 160 °C (▲); reaction conditions: 2.5% Au + 2.5% Pd/TiO_{2IMP} (25 mg), benzyl alcohol (40 ml), O_2 10 bar, stirrer speed 1500 rpm.

3. Results and discussion

3.1. Reactions using 2.5% Au + 2.5% Pd/TiO_{2IMP}

3.1.1. The effect of temperature on benzyl alcohol oxidation

The effect of reaction temperature was investigated and the results are shown in Table 1 and Figs. 1 and 2. The conversion and turnover frequency (TOF) increase with temperature and the selectivities towards benzaldehyde selectivity decreases as the

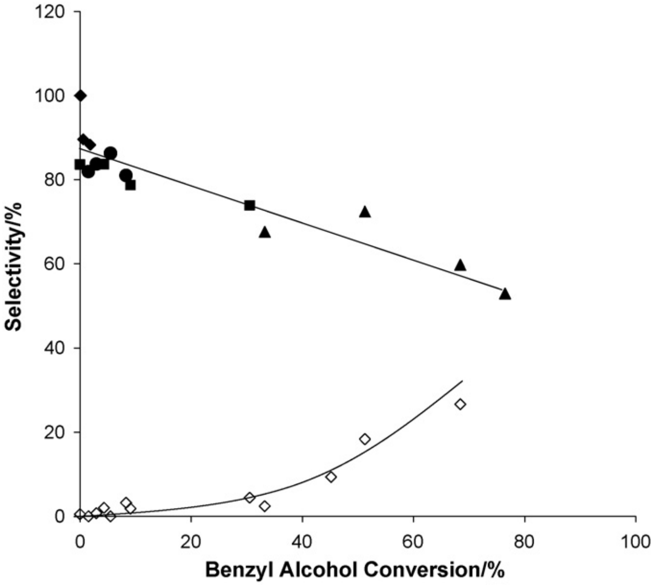

Fig. 2. The selectivity towards benzaldehyde (closed symbols) and benzoic acid (open symbols) at 100 °C (♦), 120 °C (■), 140 °C (●) and 160 °C (▲) in terms of the conversion of benzyl alcohol; reaction conditions: 2.5% Au + 2.5% Pd/TiO_{2IMP} (25 mg), benzyl alcohol (40 ml), O_2 10 bar, stirrer speed 1500 rpm.

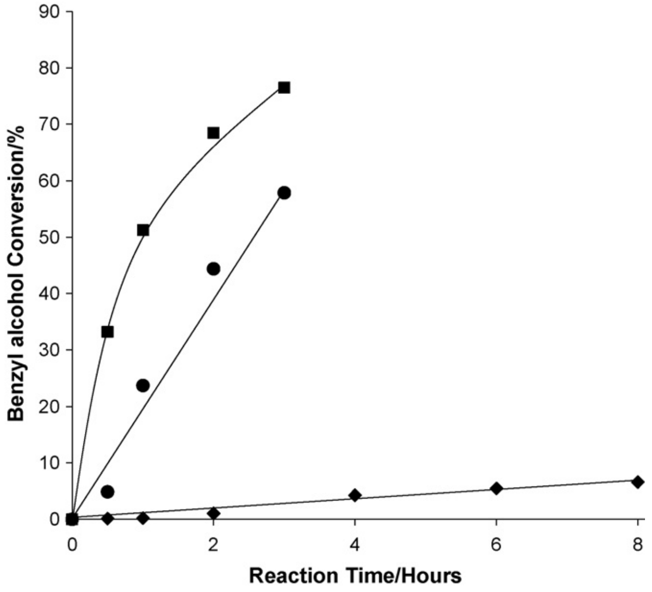

Fig. 3. The effect of oxygen pressure on the conversion of benzyl alcohol. Key: O_2 pressure of 1 bar (♦), 5 bar (●) and 10 bar (■); reaction conditions: 2.5% Au + 2.5% Pd/TiO_{2IMP} (25 mg), benzyl alcohol (40 ml), 160 °C, stirrer speed 1500 rpm.

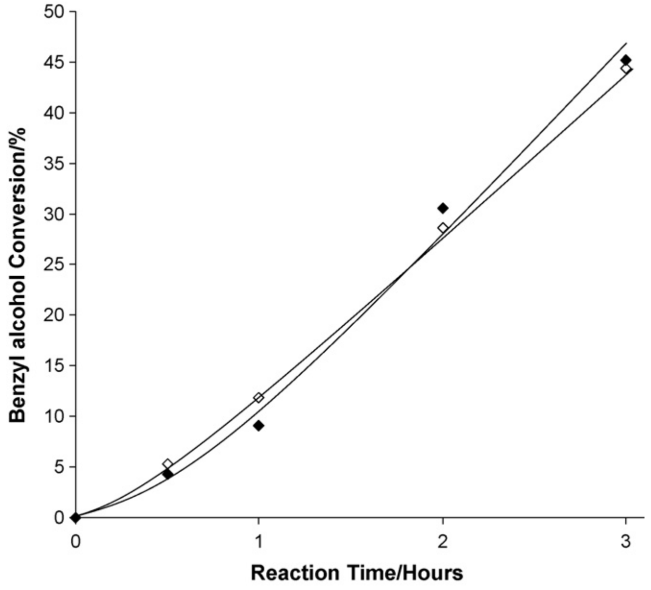

Fig. 5. The oxidation of benzyl alcohol using 2.5% Au + 2.5% Pd/TiO_{2IMP}. Key: fresh catalyst (◊) and used catalyst (♦); reaction conditions: catalyst (25 mg) benzyl alcohol (40 ml), 140 °C, 10 bar O_2, stirred at 1500 rpm.

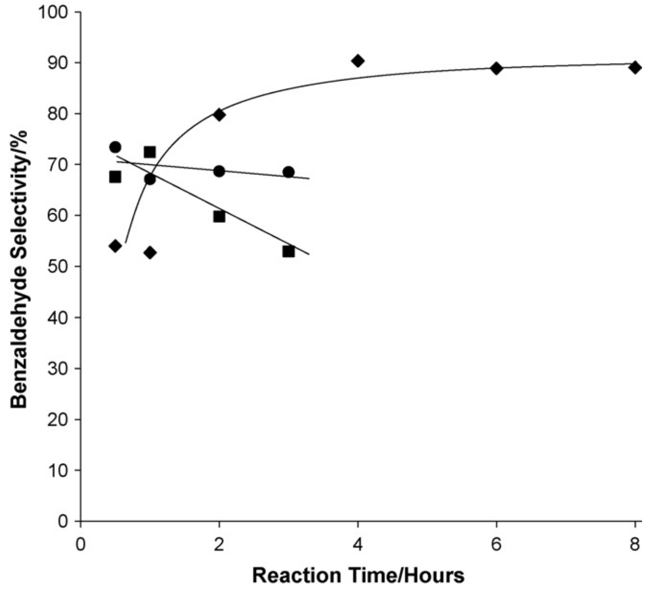

Fig. 4. The effect of oxygen pressure on the selectivity towards benzaldehyde. Key: O_2 pressure 1 bar (♦), 5 bar (●) and 10 bar (■); reaction conditions: 2.5% Au + 2.5% Pd/TiO_{2IMP} (25 mg), benzyl alcohol (40 ml), 160 °C, stirrer speed 1500 rpm.

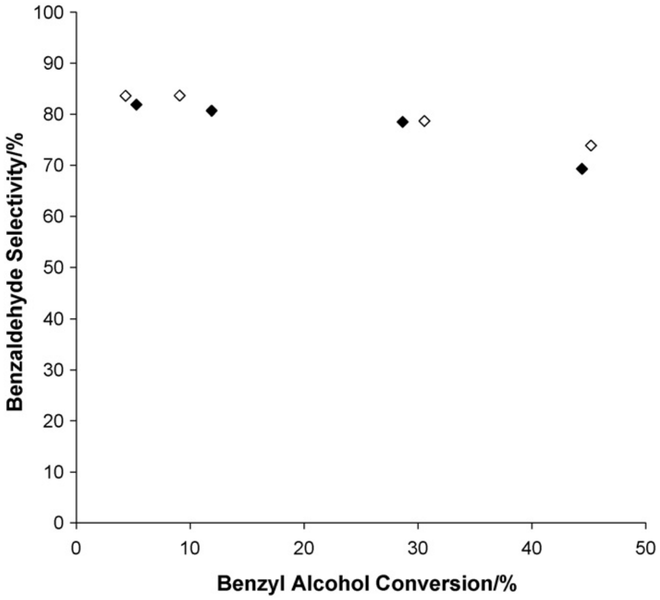

Fig. 6. The selectivity towards benzaldehyde during the oxidation of benzyl alcohol using 2.5% Au + 2.5% Pd/TiO_{2IMP}. Key: fresh catalyst (◊) and used catalyst (♦); reaction conditions: catalyst (25 mg) benzyl alcohol (40 ml), 140 °C, 10 bar O_2, stirred at 1500 rpm.

temperature is raised while the selectivity towards benzoic acid increases. However, if these selectivities are considered instead in terms of the reaction conversion (Fig. 2) then it is clear that the reactions are following the same profile, independent of temperature.

3.1.2. *The effect of oxygen pressure on benzyl alcohol oxidation*

Increasing the oxygen partial pressure had a strong influence on the rate of reaction (Fig. 3) and also showed a marked effect on the selectivity to benzaldehyde with the selectivity decreasing with increasing oxygen pressure (Fig. 4). In view of this, reactions were carried out at a lower temperature of 140 °C in order to decrease the degree of over-oxidation of the desired benzaldehyde product. Under these latter conditions, the catalyst was found to be re-usable and the conversion results for a fresh catalyst and a re-used catalyst after an initial reaction are shown in Fig. 5. The selectivity for the fresh and re-used catalysts was also found to be very similar at *ca.* 80% benzaldehyde formation (Fig. 6).

3.2. *Reactions using 2.5% Au + 2.5% Pd/TiO_{2DP}*

Benzyl alcohol oxidation (140 °C, 10 bar O_2) was investigated with the 2.5% Au + 2.5% Pd/TiO_{2DP} catalyst. The results for both the fresh and once-used catalysts are shown in Fig. 7. The activity of this catalyst is considerably higher than that of the catalyst prepared by co-impregnation (Fig. 5). The use of the catalyst for a second time leads to a small decrease in the activity. The selectiv-

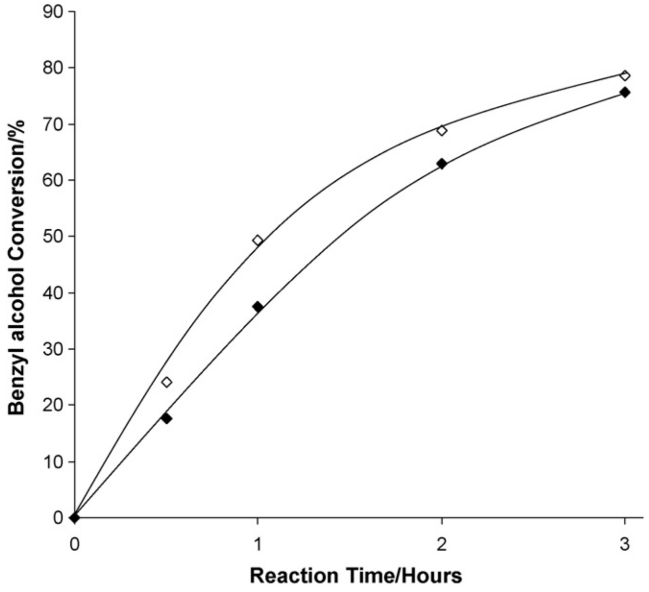

Fig. 7. The oxidation of benzyl alcohol using 2.5% Au + 2.5% Pd/TiO_{2DP}. Key: fresh catalyst (◊) and used catalyst(♦); reaction conditions: catalyst (25 mg) benzyl alcohol (40 ml), 140 °C, 10 bar O_2, stirred at 1500 rpm.

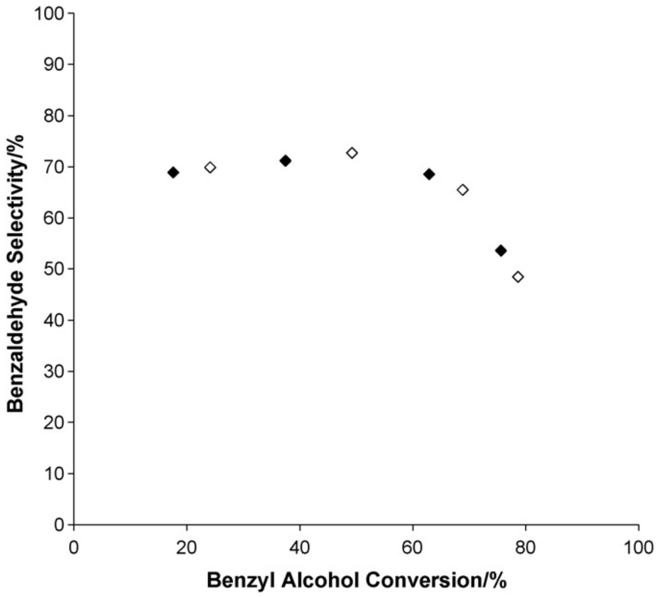

Fig. 8. The selectivity towards benzaldehyde during the oxidation of benzyl alcohol using 2.5% Au + 2.5% Pd/TiO_{2DP}. Key: fresh catalyst (◊) and used catalyst (♦); reaction conditions: catalyst (25 mg) benzyl alcohol (40 ml), 140 °C, 10 bar O_2, stirred at 1500 rpm.

ity towards benzaldehyde for the fresh and used catalysts is shown as a function of benzyl alcohol conversion in Fig. 8. The selectivities of the fresh and used 2.5% Au + 2.5% Pd/TiO_{2DP} catalyst are seen to be very similar, although it is significantly lower than that observed with 2.5% Au + 2.5% Pd/TiO_{2IMP} material. As the used catalyst showed some de-activation on use, in contrast 2.5% Au + 2.5% Pd/TiO_{2DP2} was found to be stable on re-use (Fig. 9) and gave similar selectivities (Fig. 10) to the 2.5% Au + 2.5% Pd/TiO_{2DP} catalyst.

A comparison of the initial activity and selectivities of the three catalysts is shown in Table 2. The deposition–precipitation method clearly gives enhanced activity and both 2.5% Au + 2.5% Pd/TiO_{2DP} and 2.5% Au + 2.5% Pd/TiO_{2DP2} catalysts exhibit very similar initial activities. It should be noted however that although the 2.5%

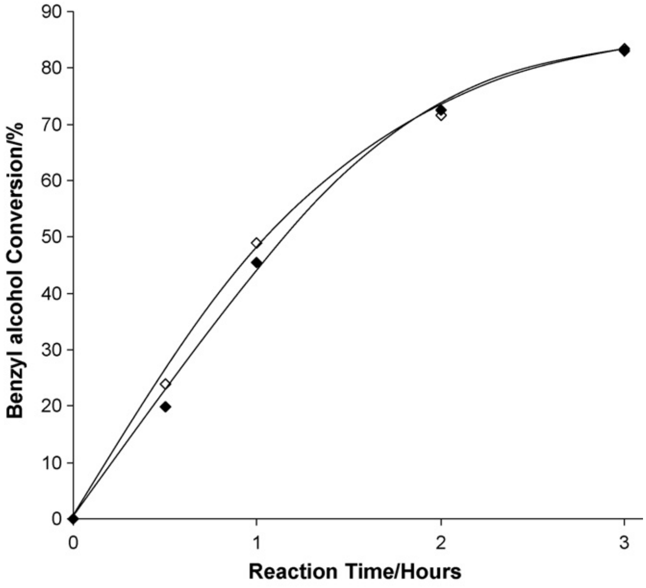

Fig. 9. The oxidation of benzyl alcohol using 2.5% Au + 2.5% Pd/TiO_{2DP2}. Key: fresh catalyst (◊) and used catalyst(♦); reaction conditions: catalyst (25 mg) benzyl alcohol (40 ml), 140 °C, 10 bar O_2, stirred at 1500 rpm.

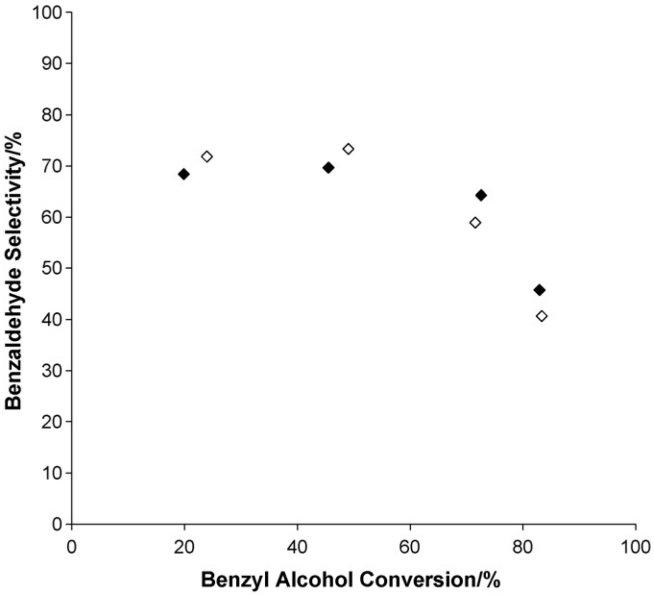

Fig. 10. The selectivity towards benzaldehyde during the oxidation of benzyl alcohol using 2.5% Au + 2.5% Pd/TiO_{2DP2}. Key: fresh catalyst (◊) and used catalyst (♦); reaction conditions: catalyst (25 mg) benzyl alcohol (40 ml), 140 °C, 10 bar O_2, stirred at 1500 rpm.

Au + 2.5% Pd/TiO_{2DP2} catalyst is more stable, it demonstrates a much lower selectivity.

3.3. Catalyst characterization

We have characterized the three sets of catalysts using transmission electron microscopy. Fig. 11(a) and (b) shows some representative bright field TEM micrographs of the unused 2.5% Au + 2.5% Pd/TiO_{2IMP} sample prepared using the impregnation method described in Section 2. In this sample a bimodal distribution of metal nanoparticles is apparent. 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

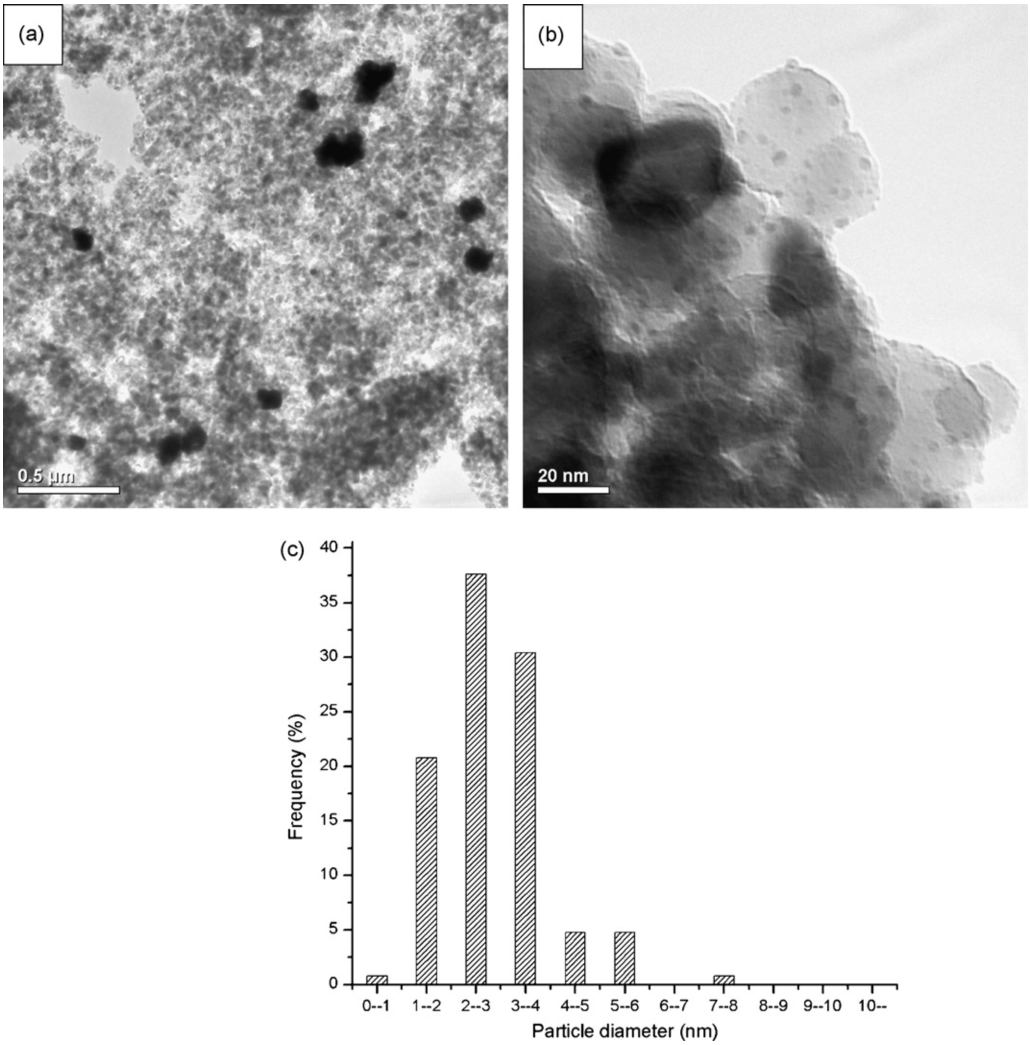

Fig. 11. Representative (a) low and (b) high magnification bright field electron micrographs of the 2.5% Au + 2.5% Pd/TiO_{2IMP} catalyst.

smaller particles which ranged between 2 and 8 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. The median size for the smaller population of Pd particles was 2.8 nm (Fig. 11(c)).

Fig. 12(a) and (b) shows some bright field TEM images of the 2.5% Au + 2.5% Pd/TiO_{2DP} catalyst before and after use, respectively. In these samples no bimodal particle size distribution was observed. All the metal nanoparticles in these samples were in the 2–10 nm size range and were found by XEDS point analyses to be AuPd alloys. The measured particle size distributions of the used and unused catalysts are shown in Fig. 12(c), where it is apparent that some particle growth has occurred after catalytic use, causing the median particle size to increase from 2.3 to 3.6 nm. This increase in particle size probably accounts for the noticeable decrease in benzyl alcohol conversion noted in Fig. 7 for the used deposition–precipitation catalyst, Bright field TEM images of the 2.5% Au + 2.5% Pd/TiO_{2DP2} catalyst before and after use are presented in Fig. 13(a) and (b), respectively. In direct contrast to the sample prepared by the impregnation method, no large Au particles were observed. In common with the other deposition–precipitation samples, all the metal nanoparticles were found by XEDS to be AuPd alloys in the 2–10 nm size range. It is interesting to note from the corresponding particle size distributions presented in Fig. 13(c), that the change in median particle size before and after use (3.7–3.9 nm) is minimal. This correlates well with the observation that the benzyl alcohol conversions for the used and unused samples were found to be very similar (see Fig. 9) for the 2.5% Au + 2.5% Pd/TiO_{2DP2} samples. Hence we conclude that the subtle change of gradually increasing the pH as opposed to keeping it constant at pH 8, during the deposition–precipitation process is enough to impart a significant difference in stability of the catalyst. It is also apparent that the much better TOF characteristics displayed by both of the sam-

Table 2
Comparison of the initial activities and selectivities for benzyl alcohol conversion.[a].

Catalyst	Conversion at 0.5 h (%)	TOF at 0.5 h (h^{-1})	Benzaldehyde selectivity (%)
2.5% Au + 2.5% Pd/TiO_{2IMP}	4.3	3690	84
2.5% Au + 2.5% Pd/TiO_{2DP}	24.1	20610	81
2.5% Au + 2.5% Pd/TiO_{2DP2}	24.0	20480	70

[a] reaction conditions: catalyst (25 mg) benzyl alcohol (40 ml), 140 °C, 10 bar O_2, stirred at 1500 rpm.

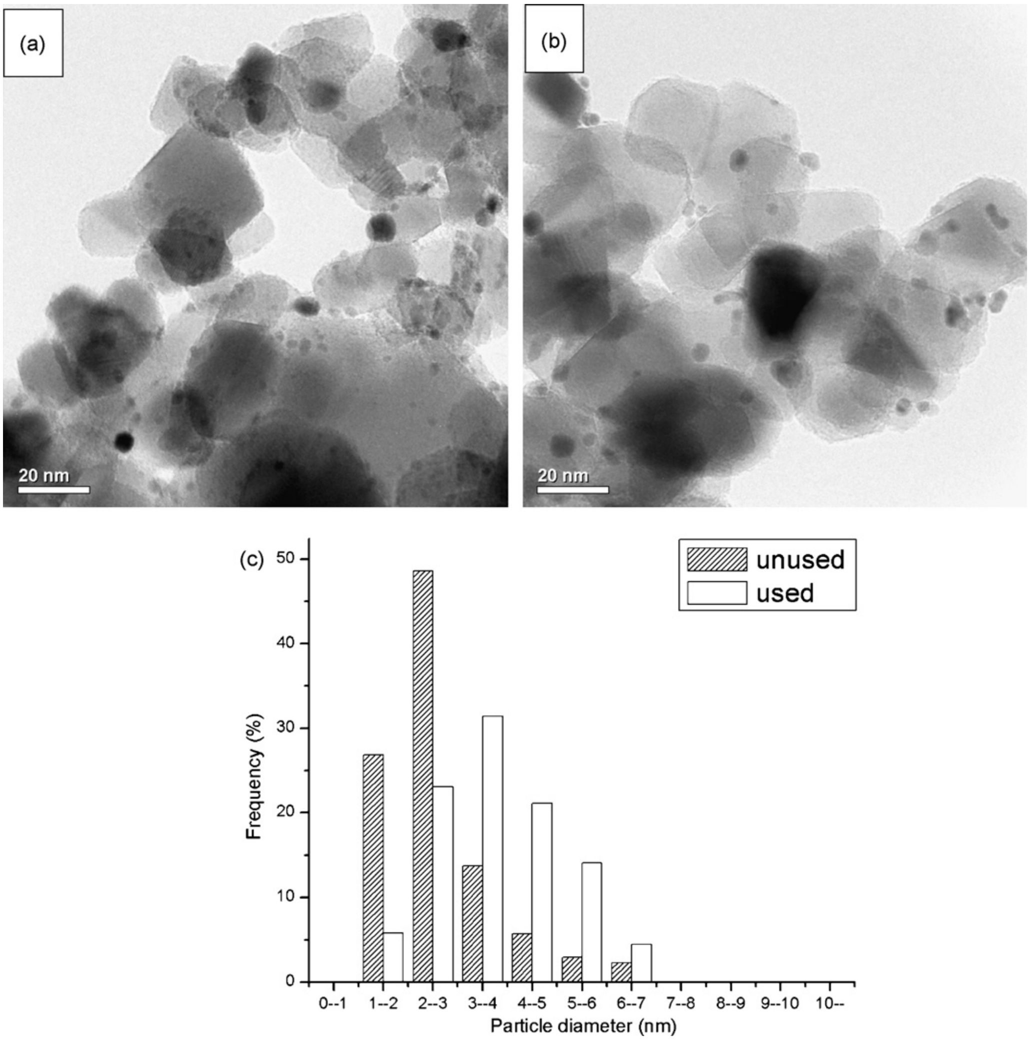

Fig. 12. Representative bright field electron micrographs of the 2.5% Au + 2.5% Pd/TiO_{2CP} catalyst (a) before and (b) after use. (c) Histogram comparing the particle size distribution of the 2.5% Au + 2.5% Pd/TiO_{2DP} catalyst before and after use.

ples prepared by deposition–precipitation (Table 3) are the result of a much higher degree of Au–Pd alloying and a considerably better Au dispersion as compared to samples made by impregnation.

In view of the enhanced activity of the catalysts prepared by deposition–precipitation, we have characterized the materials prepared using this method with XPS and this data was used to derive surface elemental compositions (at.%) which are summarized in Table 3. Data are presented for the dried materials before calcination for the fresh calcined catalyst and the catalyst after use. In addition some data is included for the catalyst which had been used a second time (the catalytic data for the second re-use were observed to be very similar to the first re-use).

The catalyst prepared whilst gradually increasing the pH of the solution (2.5% Au + 2.5% Pd/TiO_{2DP2}) shows significantly higher Pd and Au surface concentration than the catalyst prepared at constant pH. This difference may arise from either a more efficient precipitation process or possibly a higher dispersion of the metal particles. The decrease in apparent metal content on calcination, especially for the sample prepared *via* an increasing pH, probably reflects sintering of the metal particles.

Of particular interest is the Pd:Au atom ratio, and specifically how this value is affected by calcination and also after the catalyst has been used for benzyl alcohol oxidation. The theoretical Pd:Au ratio in the Au–Pd catalysts is 1:1 by weight, which is equivalent to an atom ratio of Pd:Au = 1.9:1. For the catalysts prepared with

Table 3
Surface elemental compositions derived from XPS for the Au–Pd/TiO_2 catalysts prepared by deposition–precipitation.

Catalyst	No. uses	Composition (at.%)					Atom ratio
		Pd	Au	Ti	O	Cl	Pd/Au*
2.5% u + 2.5% d/TiO_{2DP} dried	0	0.86	0.18	28.2	70.4	0.32	4.4
2.5% u + 2.5% d/TiO_{2DP} calcined	1	0.69	0.17	25.5	73.7	<0.2	3.5
2.5% u + 2.5% d/TiO_{2DP} calcined	2	0.72	0.21	25.2	73.9	<0.2	3.0
2.5% u + 2.5% d/TiO_{2DP2} dried	0	1.28	0.47	28.3	69.5	0.48	2.3
2.5% u + 2.5% d/TiO_{2DP2} calcined	0	0.84	0.25	28.6	69.7	0.62	3.0
2.5% u + 2.5% d/TiO_{2DP2} calcined	1	0.74	0.23	25.8	73.0	<0.2	2.8
2.5% u + 2.5% d/TiO_{2DP2} calcined	2	0.59	0.16	24.8	74.5	<0.2	3.3

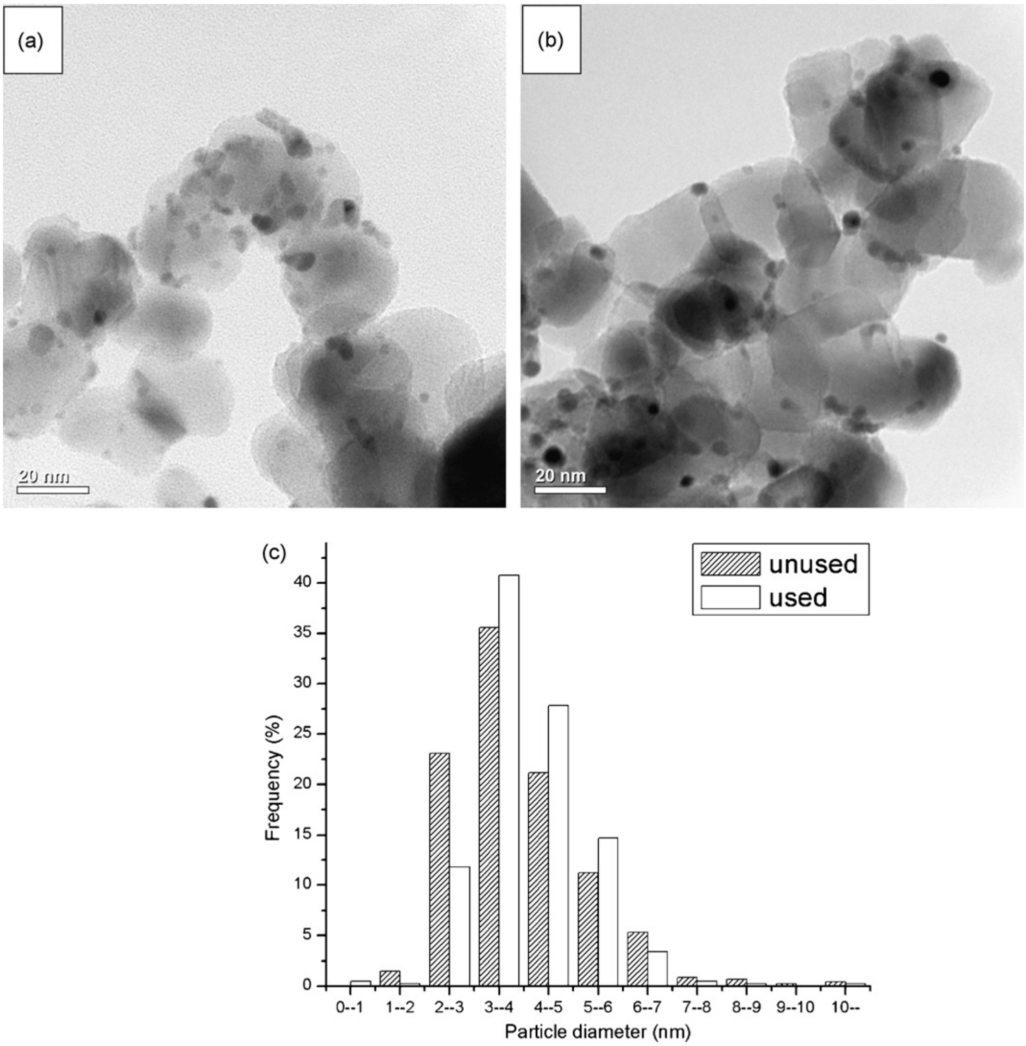

Fig. 13. Representative bright field electron micrographs of the 2.5% Au + 2.5% Pd/TiO_{2CP2} catalyst (a) before and (b) after use. (c) Histogram comparing the particle size distribution of 2.5% Au + 2.5% Pd/TiO_{2DP2} before and after use.

increasing pH (2.5% Au + 2.5% Pd/TiO_{2DP2}) the Pd:Au ratio for the dried material is 2.3, which is not too dissimilar from the theoretical value. However after calcination this ratio increases to 3.0 and remains close to this value even after reaction with benzyl alcohol. The increase over the value expected for homogeneous alloy particles or equally dispersed monometallic Pd and Au particles, may reflect particle size changes on calcination or possibly the formation of some Au-core/Pd-shell particles, which have been observed previously in some of the materials prepared using co-impregnation [31]. It is possible that the subtle differences in the surface Pd:Au ratios for the two deposition–precipitation materials may account for the differences in selectivity observed.

In conclusion it is apparent that Au:Pd catalysts prepared by deposition–precipitation are more active as catalysts for benzyl alcohol oxidation when compared with catalysts prepared by impregnation. This is due to the precipitation methodology giving a smaller particle size distribution of Au:Pd alloy nanoparticles.

Acknowledgements

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