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Selective oxidation using supported gold bimetallic and trimetallic nanoparticles

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ABSTRACT

Supported gold nanoparticles are highly effective for a range of redox reactions. In these reactions the activity is often enhanced by the addition of a second or indeed a third metallic component. A model reaction that is often investigated is the selective oxidation of benzyl alcohol using molecular oxygen as terminal oxidant. In the presence of a solvent the complexity of this reaction can often be missed. However, in the solvent-free oxidation of benzyl alcohol to benzaldehyde using supported gold palladium nanoparticles as catalysts, there are two pathways to the principal product, benzaldehyde. One is the direct catalytic oxidation of benzyl alcohol to benzaldehyde by O_2, while the second is the disproportionation of two molecules of benzyl alcohol to give equal amounts of benzaldehyde and toluene. The formation of toluene is an unwanted side reaction. In this paper the research on this reaction will be reviewed and two strategies described that can be used to switch off the formation of the non desired toluene. The first involves the use of basic supports for the gold palladium nanoparticles, which is highly effective in suppressing the formation of toluene and this may be related to the morphology of the gold palladium nanoparticles and their interaction with the support. The second involves the introduction of platinum to the gold palladium nanoparticles which also switches off toluene formation on supports that permit toluene formation in the absence of platinum. This effect may be related to the relative stability of platinum hydride.

Introduction

Interest in catalysis by supported gold and gold palladium nanoparticles continues to grow year on year in view of its great potential in the development of environmentally benign processes. This has led to the discoveries of gold and gold palladium based catalysts for the direct synthesis of H_2O_2 from H_2 and O_2 [1], epoxidation of alkenes [2,3], and oxidation of alcohols [4–7] and polyols [8,9].

In terms of catalytic transformations oxidation is of fundamental importance as it provides a means for functional group transformation in general organic synthetic methodologies [10]. However, oxidations can be difficult to control as the processes typically involve radical species and often this leads to low selectivity for the required product. While molecular oxygen is considered to be the most desirable terminal oxidant, many oxidations cannot be carried out selectively with this oxidant and often relatively expensive and toxic stoichiometric reagents are used leading to low atom efficiency [11–13]. Selective oxidation catalysis therefore requires significant development and this is in contrast to selective hydrogenation with molecular hydrogen which is widely conducted at both the laboratory and commercial scale [14]. It is known that supported gold and palladium nanoparticles show considerable promise as recyclable heterogeneous catalysts for oxidations using molecular oxygen. In this paper aspects of the selective oxidation of benzyl alcohol will be reviewed and in particular aspect of the nature of the oxidative and non-oxidative pathways to benzaldehyde will be considered. This work forms part of a facet of a plenary lecture delivered at the World Congress on Oxidation Catalysis in 2013.

Comments on the selective oxidation of benzyl alcohol

Among the alcohols, benzyl alcohol is one of the most studied examples for the selective oxidation to aldehydes [4,15]. Benzyl alcohol undergoes a variety of reactions depending on the reaction conditions and the nature of the catalyst used. The reactions reported so far are (a) oxidation to form benzaldehyde, benzoic acid, and benzyl benzoate [16] (b) disproportionation to form benzaldehyde, toluene and water [17], (c) dehydration to form dibenzylether [18] and (d) self-condensation (benzylation) to form anthracene and stilbene [19]. Many reactions are active only under particular

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reaction conditions for example, condensation to form anthracene and stilbene are found to be active at higher temperatures in the vapour phase [19]. In the low temperature liquid phase oxidation of benzyl alcohol, depending on the reaction conditions and catalysts used, many products including benzoic acid, benzyl benzoate, dibenzyl ether and toluene have been reported to be formed besides the main product benzaldehyde [20]. A clear understanding of the mechanism of the formation of all these products is necessary to fine-tune the catalyst for the selective formation of the desired product, benzaldehyde. It has been generally accepted that benzaldehyde forms by the oxidation of benzyl alcohol in the presence of an oxidant; benzaldehyde on further oxidation then leads to the formation of benzoic acid and the next product benzyl benzoate is formed either by the reaction between benzoic acid and benzyl alcohol or by the oxidation of a hemiacetal [20]. Toluene is the other major product and as roughly equimolar amounts of toluene and benzaldehyde were produced from benzyl alcohol using Au–Pd catalyst in a helium atmosphere, it has been proposed that a disproportionation of two moles of benzyl alcohol to be the origin of toluene as shown below [17].

$$2\,PhCH_2OH \rightarrow PhCHO + PhCH_3 + H_2O \qquad \text{(Scheme1)}$$

Given an understanding of the route by which the non-desired toluene product is formed could permit the identification of reaction conditions that facilitate the “switching off” of this reaction.

Oxidation of benzyl alcohol using supported gold palladium catalysts

Supported nanoparticles of metals can be very active for the selective oxidation of alcohols and both monometallic gold and palladium, as well as bimetallic gold palladium alloys [4] have been shown to be effective. There is much interest in the different ways in which supported nanoparticles can be synthesised. In general the following methods can be typically used:

(a) *Impregnation:* In this case suitable salts are impregnated with a solution containing the metals at the required concentration. This method is the easiest but produces a very broad range of particle sizes, typically 5–25 nm with much larger nanoparticles being observed. Hence this method does not disperse the metals particularly well. However, this method can produce catalysts that are very active for alcohol oxidation [4].
(b) *Deposition precipitation:* In this method the support is suspended in a solution of the metal salts and a base is added to precipitate the nanoparticles onto the pre-formed support. This method can produce a reasonably narrow particle size distribution, typically 1–10 nm.
(c) *Co-precipitation:* In this method a solution containing the metal salts and the support precursor is reacted with a base to precipitate the metal nanoparticles or their precursors simultaneously with the support. This method can also produce a reasonably narrow particle size distribution, typically 1–10 nm.
(d) *Sol-immobilisation:* In this method metal salts are dissolved in water. A stabilising agent is added and then a reducing agent to form a colloidal sol. A support is then added to form the final catalyst. This method can produce a very narrow particle size distribution, typically 4–6 nm [21].

We have found that catalysts prepared by sol-immobilisation are very effective for the oxidation of benzyl alcohol [21,22]. A 1%(Au–Pd)/TiO_2 catalyst was prepared by a sol-immobilisation method [15,21], and this was used for solvent-free oxidation of benzyl alcohol (Fig. 1). Initially, benzyl alcohol conversion increases steeply and then reaches a near plateau at approximately 70% conversion. The product mixture, at all times, comprises benzaldehyde (approx. 75%), toluene (approx. 23–24%) and a minor amount of benzoic acid. The other possible products, namely benzene, benzyl benzoate and dibenzyl ether are either observed at a trace level of less than 0.5% or are not observed under these experimental conditions. Benzaldehyde, the major product, is formed by the oxidation of benzyl alcohol and toluene is formed by the disproportionation of benzyl alcohol. Therefore, there are two active reactions in the overall oxidation of benzyl alcohol. As benzaldehyde is formed from the disproportionation and the oxidation reactions, its formation cannot be used to quantify either the oxidation or the disproportionation reactions. Toluene is formed exclusively from disproportionation; therefore the amount of toluene formed can be used as a measure of the extent of the disproportionation reaction. According to Scheme 1, the number of moles of benzyl alcohol consumed in disproportionation is twice the number of moles of toluene formed. From this value, a disproportionation turnover number (TON_D) can be calculated using Eq. (1).

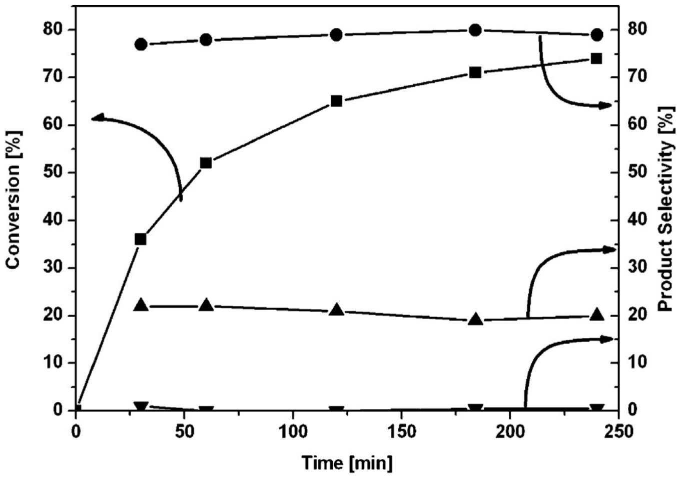

Fig. 1. Oxidation of benzyl alcohol using 1%(Au–Pd)/TiO_2 under 1 bar O_2 (relative) pressure at 393 K; substrate to metal molar ratio: 14,000; benzyl alcohol: 18.5 mmol; key ■: benzylalcohol molar conversion; ●: benzaldehyde selectivity; ▲: toluene selectivity; ▼: benzoic acid selectivity.

$$TON_D = \frac{2 \times mol_{Tol}}{mol_{Metal}} \qquad (1)$$

TON_D is used to represent the disproportionation reaction quantitatively in this paper. Benzaldehyde is formed from both the reactions; the moles of benzaldehyde formed by disproportionation is equal to the number of moles of toluene formed. By subtraction, the moles of benzaldehyde formed by the oxidation reaction can then be calculated and converted into an oxidation turnover number (TON_O) using Eq. (2)

$$TON_O = \frac{(mol_{BCHO} - mol_{Tol})}{mol_{Metal}} \qquad (2)$$

The TON_O parameter is used for the quantitative representation of the oxidation reaction in this paper. Using Eqs. (1) and (2), TON_O and TON_D values can be calculated for the data presented in Fig. 1 and these are shown in Fig. 2. The TON_{Tot} represents the overall reaction, calculated from the moles of benzyl alcohol consumed and the moles of the metals contained in the catalyst. It is clear that the disproportionation reaction is very significant using this support.

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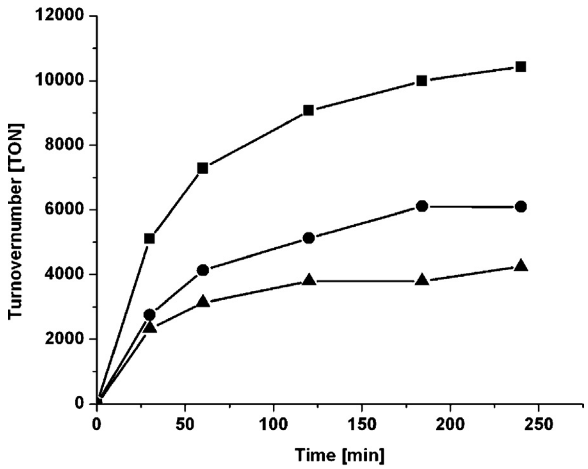

Fig. 2. Time on line profile of the turn over numbers (TON_D and TON_O) corresponding to the oxidation and disproportionation reactions, respectively, in the oxidation of benzyl alcohol using 1%(Au–Pd)/TiO_2 under 1 bar (relative) O_2 pressure at 393 K; substrate versus metal molar ratio: 14,000; benzyl alcohol: 18.5 mmol; key ■: TON_{Tot}; ●: TON_O; ▲: TON_D.

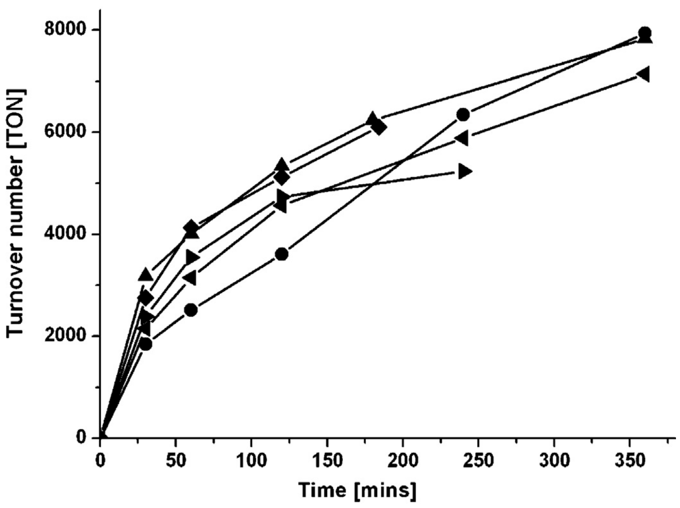

Fig. 4. Time on line profile of the TON_O calculated for the oxidation of benzyl alcohol using different catalysts at 393 K under 1 bar (relative) O_2 substrate versus metal molar ratio: 14,000; benzyl alcohol: 18.5 mmol; key ●: 1%(Au–Pd)/C ▲: 1%(Au–Pd)/TiO_2; ◀: 1%(Au–Pd)/Nb_2O_5; ♦: 1%(Au–Pd)/ZnO; ▶: 1%(Au–Pd)/MgO.

Switching off toluene formation by using different support materials

Au–Pd nanoparticles were supported on a variety of different supports including Nb_2O_5, activated carbon, MgO and ZnO using sol-immobilisation. Benzyl alcohol oxidation was carried out using all these catalysts and the results are shown in Fig. 3. Under these reaction conditions the supports themselves were found to be inactive. The data indicates that Au–Pd supported on activated carbon is the most active catalyst followed by the TiO_2 and Nb_2O_5 supported catalysts. The MgO and ZnO supported catalysts exhibited the least activity for the reaction. However, the catalysts are all fairly active for this reaction but the selectivity for these five catalysts are very different. Activated carbon-, TiO_2-, and Nb_2O_5-supported catalysts formed toluene as a major by-product, whereas MgO and ZnO supported catalysts did not produce any toluene. For these latter two catalysts, benzaldehyde was the only major product with selectivity in excess of 99%. Hence by simply changing the catalyst support, we can either switch on or switch off the disproportionation reaction. The turnover numbers for the oxidation and disproportionation reactions are quite revealing (Figs. 4 and 5). TON_O values for all these catalysts were found to be more or less equivalent, with only very small deviations (Fig. 4). This implies that the oxidation reaction is effectively independent of the identity of the support. However, this is not the case for the disproportionation reaction since only with MgO- or ZnO-supported catalysts is this not observed. Analysis of the data in Figs. 3–5 it can be concluded that the increased activity is due to the difference in the activity for the disproportionation reaction and not because of the oxidation reaction. This is an important result and to determine the origin of the effect detailed STEM studies have been conducted. While no major differences were observed in the particle size distribution for these five catalysts (Fig. 6), and the particle size distributions were mainly in the 3–8 nm range, and this can be expected since the catalysts are all derived from the same colloidal sol. However, there were clear differences observed in the way in which the nanoparticles interact with the support (Fig. 7) since the support controls the degree of wetting. On MgO, ZnO and TiO_2 the AuPd nanoparticles have a tendency to wet the

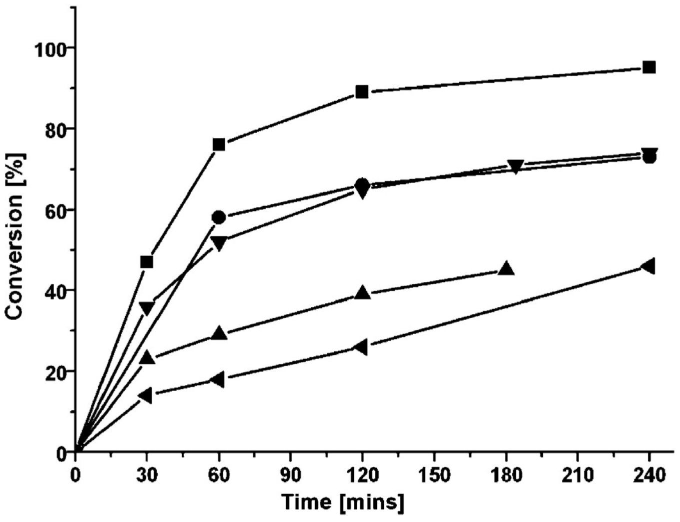

Fig. 3. Kinetic profile for the oxidation of benzyl alcohol using different supported Au–Pd catalysts under 1 bar (relative) O_2 at 393 K; substrate versus metal molar ratio: 14,000; benzyl alcohol: 18.5 mmol; key ■: 1%(Au–Pd)/C; ▲: 1%(Au–Pd)/ZnO; ▼: 1%(Au–Pd)/TiO_2; ◀: 1%(Au–Pd)/MgO; ●: 1%(Au–Pd)/Nb_2O_5.

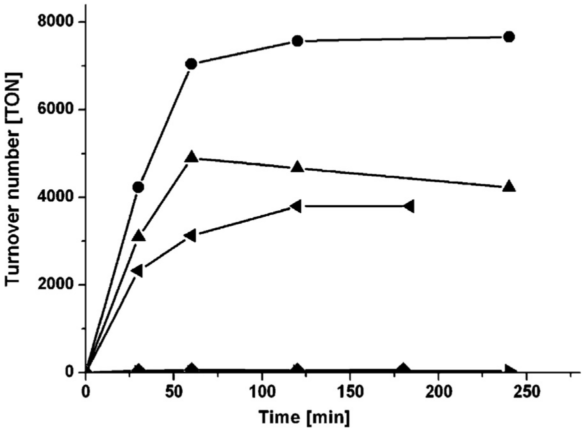

Fig. 5. Time on line profile of the TON_D number calculated for the oxidation of benzyl alcohol using different catalysts at 393 K under 1 bar (relative) O_2; substrate versus metal molar ratio: 14,000; benzyl alcohol: 18.5 mmol; key ■: 1%(Au–Pd)/ZnO; ▲: 1%(Au–Pd)/Nb_2O_5; ▼: 1%(Au–Pd)/MgO; ◀: 1%(Au–Pd)/TiO_2; ●: 1%(Au–Pd)/C. It should be noted that no toluene is formed for the ZnO- and MgO-supported samples.

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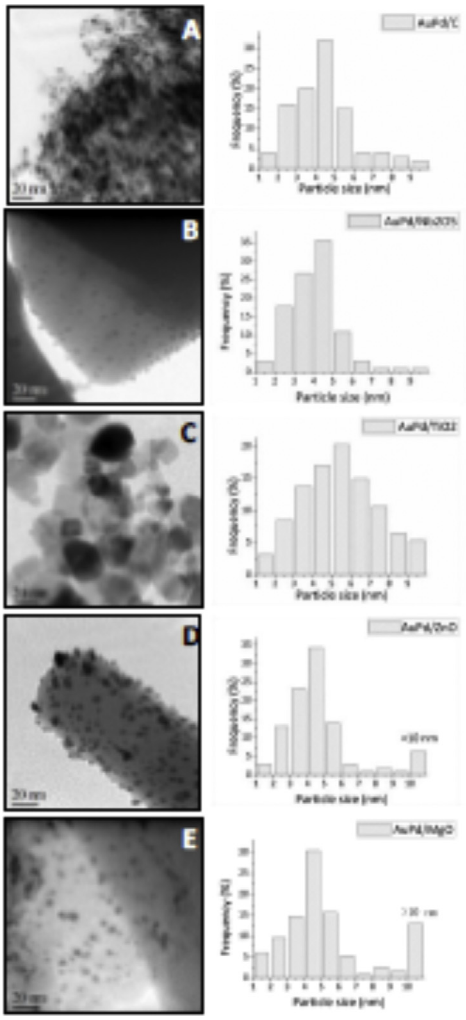

Fig. 6. Pairs of TEM images (left) and particle size distributions (right) of the catalysts (A): 1%(Au–Pd)/C; (B): 1%(Au–Pd)/TiO_2; (C): 1%(Au–Pd)/Nb_2O_5; (D): 1%(Au–Pd)/ZnO and (E): 1%(Au–Pd)MgO.

support as evidenced by particle flattening and surface faceting, as well as the development of an extended intimate particle/support interface. For these catalysts there is an enhanced influence of the interfacial sites. With Nb_2O_5 and activated carbon as supports the AuPd particles retain a roughly spherical shape. As noted earlier, the activity for the disproportionation reaction follows the trend:

$$\text{Activatedcarbon} > Nb_2O_5 > TiO_2 > MgO = ZnO$$

which is opposite for the trend observed for wetting of the support, i.e.

$$MgO = ZnO > TiO_2 > Nb_2O_5 > \text{activatedcarbon}$$

Hence by controlling the nature of these interfacial sites it is possible to switch off the non-desired formation of toluene by the non-oxidative disproportionation pathway.

Switching off toluene formation using supported gold palladium platinum trimetallic nanoparticles

Recently, we have investigated the oxidation of benzyl alcohol using supported trimetallic nanoparticles [23]. Supported Au–Pd–Pt trimetallic catalysts were synthesised by the sol-immobilisation method. This process involved the co-reduction of three metal precursors ($HAuCl_4$, $PdCl_2$ and H_2PtCl_6) at the desired concentration in aqueous solutions, using sodium borohydride as chemical reductant and poly vinyl alcohol (PVA) as the protective ligand. The colloids were then immobilised onto an activated carbon support, followed by a washing and 120 °C drying process to yield the final catalysts with 1 wt% total metal loading. For comparative purposes Au-only, Pd-only, Pt-only catalysts, as well as Au–Pd, Au–Pt and Pt–Pd bimetallic catalysts were also prepared using a similar sol-immobilisation procedure.

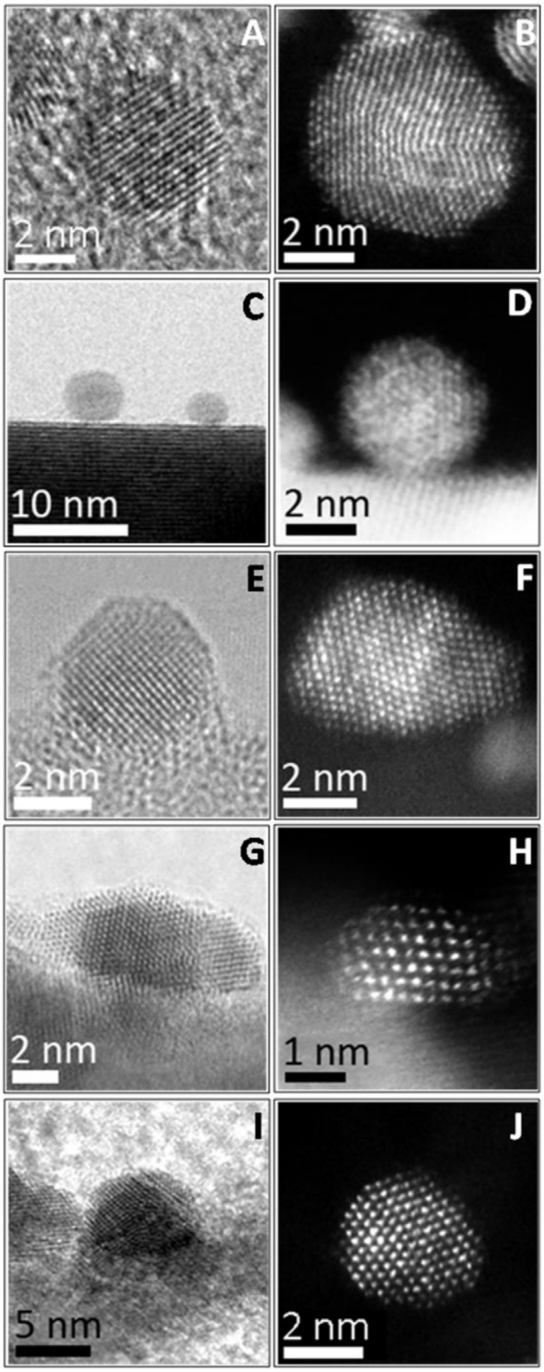

Fig. 7. Pairs of HREM images (left) and STEM images (right) of the catalysts (A) and (B): 1%(Au–Pd)/C; (C) and (D): 1%(Au–Pd)/TiO_2; (E) and (F): 1%(Au–Pd)/Nb_2O_5; (G) and (H): 1%(Au–Pd)/ZnO and (I) and (J): 1%(Au–Pd)MgO.

Oxidations were carried out in a stirred autoclave reactor using solvent free conditions (40 ml of benzyl alcohol), at 120–140 °C, and $pO_2 = 10$ bar. The catalytic results are given in Table 1 presents for

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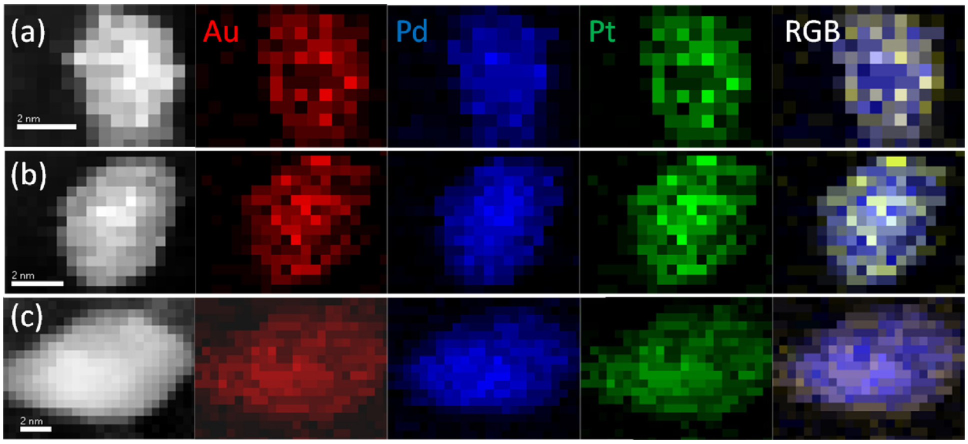

Fig. 8. STEM–XEDS spectrum image analysis of the 1 wt% (0.3Au–0.4Pd–0.3Pt)/C trimetallic sample. The first column shows HAADF images from representative particles that are (a) ~3 nm, (b) ~5 nm, and (c) ~10 nm in size. The scale bar represents 2 nm. The next three columns show the corresponding XEDS maps derived from the Au L (9.64–9.84 keV), Pd L (2.75–3.05 keV) and Pt L (9.35–9.55 keV) peaks. The final column shows the corresponding RGB overlay maps where Au is red, Pd is green and Pt is blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Comparison of benzyl alcohol oxidation at iso-conversion of 30% with Pd-only, Au–Pd and various Au–Pd–Pt catalysts supported on carbon prepared by the sol-immobilisation method.

Catalyst	Selectivity (%)			
	Toluene	Benzaldehyde	Benzoic acid	Benzyl benzoate
1%(0.65Au/0.35Pd)/C	8.1	80.5	2.6	8.8
1%(0.5Au/0.5Pd)/C	6.9	81.5	3.6	8.0
1%(0.3Au/0.4Pd/0.3Pt)/C	0.8	85.7	6.5	7.0
1%(0.4Au/0.4Pd/0.2Pt)/C	0.6	83.3	6.8	9.3
1%(0.45Au/0.45Pd/0.1Pt)/C	0.4	86.7	5.9	7.0
1%Pd/C	5.6	78.7	5.8	9.9

isoconversion of benzyl alcohol of 30%. As noted in the previous section the oxidation of benzyl alcohol with O_2 under solvent-free conditions proceeds efficiently with very high catalytic activity using carbon-supported Au–Pd nanoparticles and the main product is benzaldehyde with the major by-product being toluene. Addition of Pt to the AuPd supported nanoparticles switches off the formation of toluene. These results clearly demonstrate that only a small amount of Pt is needed for the effective termination of toluene formation. We consider the effect is due to the relative stability of platinum hydride in comparison with palladium hydride and it is this enhanced stability that leads to the reduction in toluene formation. Detailed characterisation of these trimetallic nanoparticles by aberration corrected scanning transmission electron microscopy showed that they comprised homogeneous trimetallic nanoalloys (Fig. 8).

Concluding comments

It is clear that the oxidation of benzyl alcohol involves two competing processes. The first is the selective oxidation pathway leading to the formation of benzaldehyde as the primary product. The second competing pathway involves a disproportion of benzyl alcohol forming both toluene and benzaldehyde. The formation of toluene can effectively be eliminated by careful design of the catalysts. Two methods have been demonstrated; one approach involves the nature of the support and basic oxides decrease the formation of toluene substantially. However, the addition of platinum to the gold palladium alloy catalysts also leads to a switching off of toluene formation on a support that gives high levels of toluene formation with the gold palladium alloy catalyst. It is probable that there may be other methodologies for controlling this non-desired pathway and this study shows the importance of catalyst design in securing highly effective selective oxidation catalysts.

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