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Oxidation of benzyl alcohol using supported gold–palladium nanoparticles

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ABSTRACT

Gold–palladium nanoparticles either in the form of colloids or supported nanoparticles have been extensively used as redox catalysts 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 either using deposition-precipitation or 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 impregnation, deposition-precipitation and colloidal methods. The catalyst materials have been evaluated for the oxidation of benzyl alcohol, as a model reaction. In addition, we have focused our attention on the utilisation of different types of reactors (autoclave versus glass reactors) and we now emphasise the possibility of using simplified types of reactors which have the advantage of significant cost savings and ease of application.

1. Introduction

The utilisation of molecular oxygen in combination with the uses of heterogeneous catalytic systems has been identified as an attractive green methodology for the production of fine chemicals in the fragrance and pharmaceutical industries. The current commercial processes are based on the use of stoichiometric inorganic oxidants such as potassium dichromate. However, these processes typically produce large amounts of waste and often result in poor atom efficiency, making them both environmentally unfriendly and ultimately non-economic [1–3]. In response, many homogeneous systems able to catalyse liquid phase oxidation have been used successfully, resulting in high product yields [4–7]. However, the disadvantage of the use of homogeneous systems is widely known to be associated with separation and recycling. Thus, interest has shifted towards the development of heterogeneous catalytic systems, which can be used in both batch and fixed-bed reactors. A variety of heterogeneous catalysts has been developed in the last decade, based on multicomponent oxides, heteropolyacids, vanadium phosphorus oxides and platinum group metals deposited on a support [8–11]. In fact, the most promising heterogeneous catalysts are currently based on platinum group metals [11–13]. However, the drawback of utilising platinum group metals individually as catalysts is that frequently poor selectivity and deactivation are often observed [12]. Using a bimetallic catalyst, thus incorporating a second metal component, activity, selectivity and catalyst lifetime can often be improved, thus minimising deactivation [11,13]. Recent studies have demonstrated the efficacy of Au, Pt and Pd derived bimetallic catalysts for the aerobic partial oxidation of alcohols and polyols [11,14–29]. In our previous papers we have shown that catalysts based on supported Au–Pd nanoparticles are effective catalysts for the oxidation of polyols and alcohols [30–34], as well as for the synthesis of hydrogen peroxide [35–39]. In this paper we examine the oxidation of benzyl alcohol using mild conditions and contrast the use of three reactor systems based either on the use of an autoclave reactor or the use of glass reactors operating at lower reaction pressures and we show that use of glass reactors can be effective. In addition, we use three methods for the preparation of Au–Pd supported catalysts namely: impregnation, sol-immobilisation and deposition-precipitation methods, which are the major methods used for the synthesis of gold based catalysts [22,40–43]. We have used the oxidation of benzyl alcohol as a model reaction and we have demonstrated previously that the catalysts can be used for the selective oxidation of a broad range of alcohols [31].

2. Experimental

2.1. Materials

$HAuCl_4 \cdot 3H_2O$ (99.99% purity) and $PdCl_2$ (99.99% purity) were supplied by Johnson Matthey, $Pd(NO_3)_2$.was supplied by Aldrich, Titania (Degussa P25) was used as the support. Na_2CO_3 (99.0% of purity), $NaBH_4$ of purity > 96% (Aldrich), polyvinylalcohol (PVA)

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(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 desired concentration, $NaBH_4$ (0.1 M) and PVA (1%, w/w) were prepared prior to the preparation of the catalytic materials.

2.2. Catalyst preparation

Bimetallic Au–Pd supported catalysts were prepared using the following three preparation methods: impregnation, deposition-precipitation using sodium carbonate and sol-immobilisation. The detailed procedures for the three preparation methods have been described in detail elsewhere [32,33,44]. Briefly, for the synthesis of Au–Pd/TiO_2 catalyst synthesised by the 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 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; *SI* denotes sol-immobilisation; *DPC* denotes deposition-precipitation using sodium carbonate; *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. Alcohol oxidation

Autoclave studies: 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 5 times with oxygen leaving the vessel at 10 bar gauge. The stirrer was set at 1500 rpm 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.

Glass reactor studies: Experiments were also performed using a glass round bottom flask fitted with a balloon pressurised with oxygen and a modified version of the commercially available carousel multi reaction system manufactured by Radleys [45]. For both of these reactors the pressure of the oxygen was 1 bar (relative). Both of the reactors were equipped with a heater, a thermometer and a magnetic stirrer. The stirrer was set at 1000 rpm (maximum stirrer speed). In a typical reaction, the requisite amount of catalyst and benzyl alcohol were charged into the reactor and reactor was purged 5 times with O_2 and the reactor was fitted directly to the O_2 line in the case of the Radleys reactor and the O_2 balloon in the case of round bottom flask. After this step the reactors were quickly mounted to the base that was preheated to the reaction temperature. In the case of reactions with the Radleys reactors, the data points in the time online graph were obtained from different reactions that were stopped at different time intervals. In the case of round bottom flask reaction, constant volume of the samples was withdrawn at regular time intervals. The samples were cooled immediately in an icebath and centrifuged to remove the solid catalyst. An aliquot of the clear supernatant reaction mixture (0.5 mL) was diluted with mesitylene (0.5 mL, external standard for GC analysis).

Samples were removed periodically and analysed by GC. 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 standard method was used.

2.4. Characterisation of catalysts

The materials prepared by impregnation and immobilisation have been extensively characterised in our previous studies using STEM-HAADF microscopy and XPS [31,33,38,39,44,46,47]. Briefly we describe here details related to their structures. Catalysts prepared by the impregnation method generate a broader particle size distribution and greater median size than the sol-immobilisation method. Specifically, catalysts synthesised by the impregnation method show that the Au–Pd/TiO_2 catalyst has particles mainly in the 2–5 nm range with *ca.* 8% of larger particles (>20 nm). STEM-XEDS [31,37,38,46,47] shows that the TiO_2-supported material has a core–shell structure with a palladium-rich shell and a gold-rich core, an observation that is infrequently observed with other oxide-supported Au–Pd catalysts prepared by wet impregnation. The reason for the formation of core–shell structures is due to the calcination procedure used with the impregnated catalysts. We have noted earlier [31] that calcination at 400 °C is required to form stable re-usable catalysts with this preparation method. During the calcinations process the Pd migrates to the surface of the nanoparticles when an oxide is used as the support.

Characterisation of catalysts prepared *via* the sol-immobilisation method has also been reported previously [33,39]. The median diameter of the sol-immobilised pure-Au are about 4.0 nm, while for pure-Pd the median size on the TiO_2 support was 3.8 nm. The median particle sizes for the sol-immobilised Au–Pd alloy were 3.8 nm on the TiO_2 support. It is also important to emphasise that the major advantage of the sol-immobilisation preparation method is that it significantly minimises the formation of larger particles (>10 nm) 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 have shown that the Au–Pd nanoparticles prepared by sol-immobilisation are homogeneous alloys [33,39]. For the bimetallic Au–Pd supported catalysts synthesised by the deposition-precipitation method using sodium carbonate it was found that the metal nanoparticles are in the 2–10 nm particle size range and consist of Au–Pd alloys with gold core–Pd shell morphology formed during the calcination process [44].

3. Results and discussion

The bimetallic Au–Pd supported catalysts were initially tested in the liquid phase oxidation of benzyl alcohol at 100 °C with 10 bar of oxygen using an autoclave reactor. For these reaction conditions we have demonstrated previously that there are no diffusion limitations [33,34]. Results are shown in Fig. 1 and Tables 1 and 2. The most active catalyst was the one prepared by the sol-immobilisation method, followed by deposition-precipitation and impregnation. Taking into account the particle size with the sol-immobilisation method, which produces the smaller particle size (around 4 nm), and a narrower particle size distribution, followed by the deposition-precipitation and impregnation methods, this was somewhat expected in terms of activity. Hence we consider that the major factor determining catalyst activity under these reaction conditions is the particle size distribution. However, the surface composition also varies with the preparation method with the Au–Pd/TiO_2 catalysts prepared by impregnation and calcination having a Pd-rich surface, but we consider this effect to be sec-

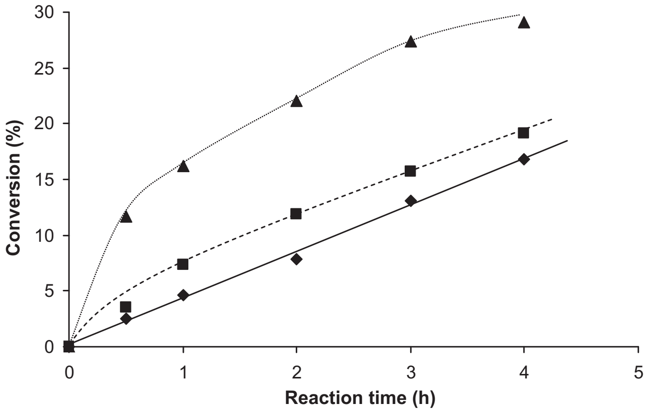

Fig. 1. Selective oxidation of benzyl alcohol using an autoclave reactor: *Reaction conditions*: benzyl alcohol, substrate/metal molar ratio = 58,580, $T = 100\,^{\circ}C$, $pO_2 = 10$ bar, reaction time = 4 h, stirring rate 1500 rpm. *Key*: ▲, benzyl alcohol conversion – 1 wt.% (Au–Pd)/TiO_{2SIm}; ■, benzyl alcohol conversion – 5 wt.% (Au–Pd)/TiO_{2DPCw}; ◆, benzyl alcohol conversion – 1 wt.% (Au–Pd)/TiO_{2Im}.

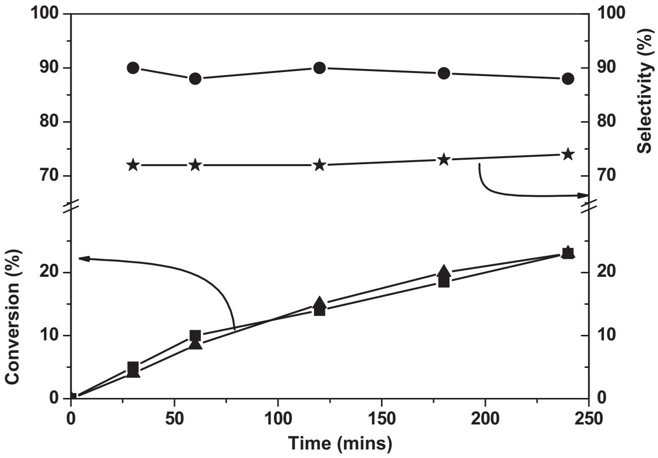

Fig. 2. Comparison of two different types of reactors: Radleys reactor versus round bottom flask reactor for the oxidation of benzyl alcohol oxidation using 1 wt.% (Au–Pd)/TiO_{2SIm} catalyst prepared by sol-immobilisation method. *Reaction conditions*: benzyl alcohol, substrate/metal molar ratio = 56,100, $T = 100\,^{\circ}C$, $pO_2 = 1$ bar, reaction time = 4 h, stirring rate 1000 rpm. *Key*: ■, benzyl alcohol conversion in the Radleys reactor; ▲, benzyl alcohol conversion in the round bottom flask; ●, benzaldehyde selectivity in the Radleys reactor; ★, Benzaldehyde selectivity in the round bottom flask.

ondary in importance with respect to the main effect of particle size. In terms of selectivity the catalysts were compared at iso-conversion level (15%) and the results are presented in Table 2. The highest selectivity to benzaldehyde was obtained with the bimetallic Au–Pd supported catalysts synthesised by sol-immobilisation, whereas the least selective was prepared by impregnation, with a substantial level of toluene formed. One possible reason for this trend could be the residual chlorine that remains on the titania during the impregnation method, therefore the increase of surface acidity could be responsible for the higher level of toluene formation. However, the catalysts prepared by impregnation also have a Pd-rich surface. We have previously studied the origin of toluene in benzyl alcohol oxidation [34] and we have shown that its formation is highly sensitive to the surface oxygen concentration and it is also facilitated by acidic surfaces and hence the Pd-rich surface may provide a more facile pathway than when more Au is present. In the other two preparation methods extensive washing with distilled water typically occur during filtration, which minimises the surface acidity.

The results above clearly demonstrate that the most active catalyst was the one synthesised by the sol-immobilisation method, and hence we investigated the possibility of performing the liquid phase oxidation of benzyl alcohol in a glass low pressure reactor, which would permit simplification of the process. The aim was to determine if oxidation reactions with molecular oxygen using the sol-immobilised catalysts could be carried out using standard laboratory equipment, as is the case for many hydrogenation reactions using hydrogen. Therefore, we investigated the use of glass reactors and selected two types of reactors, one based on a round bottom flask fitted with a balloon filled with oxygen and the other one based on a Radleys glass reactor fitted with a cap and the ability to pressurise the reactor at low pressure (maximum 3 bar).

The comparison of the three different types of reactors is shown in Tables 3 and 4. It is worth to note that in terms of TOF (turnover frequency) similar catalytic activity was observed in all the cases (Table 3). In Fig. 2, the reactions carried out using the Radleys and round bottom flask reactors are shown. An increase of conversion was accompanied by a slight decrease in the selectivity to benzaldehyde, whereas the formation of consecutive products such as benzoic acid and benzyl benzoate were below 1%. The major by-product was toluene. In terms of selectivity, compar-

Table 1
Benzyl alcohol oxidation after 4 h reaction with Au–Pd catalysts prepared by impregnation, deposition-precipitation and sol-immobilisations methods.[a]

Entry	Catalyst	Conv. (%)	Selectivity (%)						
			Benzaldehyde	Benzoic acid	Benzyl benzoate	Toluene	DBE[b]	Benzene	TOF (h^{-1}) [c]
1	1%(Au–Pd)/TiO_{2Im}	16.8	70.6	0.4	1.1	27.9	0.0	0.0	2940
2	5%(Au–Pd)/TiO_{2DPCw}	19.2	80.6	0.5	2.0	16.8	0.0	0.1	4180
3	1%(Au–Pd)/TiO_{2SIm}	29.1	91.6	0.6	1.0	6.7	0.0	0.1	136,700

[a] *Reaction conditions*: benzyl alcohol, substrate/metal molar ratio = 58,580, $T = 100\,^{\circ}C$, $pO_2 = 10$ bar, reaction time = 4 h, stirring rate 1500 rpm.
[b] DBE = dibenzyl ether.
[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 2
Benzyl alcohol oxidation results at iso-conversion for Au–Pd catalysts prepared by impregnation, deposition-precipitation and sol-immobilisation methods.[a]

Entry	Catalyst	Conv. (%)	Selectivity (%)					
			Benzaldehyde	Benzoic acid	Benzyl benzoate	Toluene	DBE[b]	Benzene
1	1%(Au–Pd)/TiO_{2Im}	15	70.6	0.4	1.2	27.8	0.0	0.0
2	5%(Au–Pd)/TiO_{2DPCw}	15	81.3	0.6	2.5	15.5	0.0	0.1
3	1%(Au–Pd)/TiO_{2SIm}	15	88.1	0.4	1.0	10.4	0.0	0.1

[a] *Reaction conditions*: benzyl alcohol, substrate/metal molar ratio = 58,580, $T = 100\,^{\circ}C$, $pO_2 = 10$ bar, reaction time = 4 h, stirring rate 1500 rpm.
[b] DBE = dibenzyl ether.

Table 3
Benzyl alcohol oxidation performance after 4 h reaction for 1 wt.% Au–Pd/TiO_{2SIm} catalysts prepared by sol-immobilisation method using three types of reactor systems.[a]

Entry	Reactor system	Conv. (%)	Selectivity (%)						
			Benzaldehyde	Benzoic acid	Benzyl benzoate	Toluene	DBE[b]	Benzene	TOF (h^{-1})[c]
1	Autoclave reactor[d]	27.0	79.7	0.2	0.4	19.6	0.0	0.1	4900
2	Radleys reactor[e]	23.0	88.0	0.1	0.8	10.7	0.2	0.2	5760
3	Round bottom flask[e]	23.0	74.0	0.2	0.4	25.0	0.4	0.0	4830

[a] *Reaction conditions*: benzyl alcohol, $T = 100\,^\circ C$, $pO_2 = 1$ bar, reaction time = 4 h.
[b] DBE = dibenzyl ether.
[c] Calculation of TOF (h^{-1}) after 0.5 h of reaction. TOF numbers were calculated on the basis of total loading of metals.
[d] Substrate/metal molar ratio = 58,580, stirring rate 1000 rpm.
[e] Substrate/metal molar ratio = 56,100, stirring rate 1000 rpm.

Table 4
Benzyl alcohol oxidation results at iso-conversion for 1 wt.% Au–Pd/TiO_{2SIm} catalysts prepared by sol-immobilisation method using three types of reactor systems.[a]

Entry	Reactor system	Conv. (%)	Selectivity (%)					
			Benzaldehyde	Benzoic acid	Benzyl benzoate	Toluene	DBE[b]	Benzene
1	Autoclave reactor[c]	15	76.7	0.2	0.6	22.4	0.0	0.1
2	Radleys reactor[d]	15	89.8	0.1	0.9	8.8	0.2	0.2
3	Round bottom flask[d]	15	72.0	0.0	0.0	28.0	0.0	0.0

[a] *Reaction conditions*: benzyl alcohol, $T = 100\,^\circ C$, $pO_2 = 1$ bar, reaction time = 4 h.
[b] DBE = dibenzyl ether.
[c] Substrate/metal molar ratio = 58,580, stirring rate 1000 rpm.
[d] Substrate/metal molar ratio = 56,100, stirring rate 1000 rpm.

ison at iso-conversion (15%) showed that the highest selectivity to benzaldehyde was observed using the Radleys reactor followed by the autoclave reactor system. The high selectivity to toluene observed with the low pressure glass reactor system can be ascribed to the lower availability of oxygen in the solution. We have shown previously that at low oxygen pressure and hence limiting oxygen concentration in the solution the toluene formation increased [33,34]. Especially, at low oxygen pressure (1 bar of oxygen) the formation of toluene and benzaldehyde are highly sensitive to the availability of the surface oxygen [34]. Nevertheless, we have demonstrated that it is possible to obtain high selectivity together with high catalytic activity using a Radleys reactor, which is pressurised and continually fed with oxygen as in the case of an autoclave reactor. It is the availability of oxygen rather than the materials of construction of the reactors evaluated which is the controlling parameter that secures high selectivity to benzaldehyde. Taking into account the above results it is important to maintain the pressure of oxygen at 1 bar continually to obtain high selectivity to benzaldehyde under the corresponding reaction conditions.

4. Conclusions

We have demonstrated that simplified glass reactors can effectively be used for the selective oxidation of benzyl alcohol with high selectivity to benzaldehyde and high catalytic activity. The utilisation of glass reactors at mild reaction conditions (low oxygen pressure and low temperature) can suppress significantly the financial cost of equipment and provide an accurate and easy way of transforming alcohols to useful chemical intermediates.

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