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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-