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Solvent-free oxidation of benzyl alcohol using titania-supported gold–palladium catalysts: Effect of Au–Pd ratio on catalytic performance

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Abstract

The oxidation of benzyl alcohol with molecular oxygen under solvent-free conditions has been investigated using a range of titania-supported Au–Pd alloy catalysts to examine the effect of the Au–Pd ratio on the conversion and selectivity. The catalysts have been compared at high reaction temperature (160 °C) as well as at 100 °C, to determine the effect on selectivity since at lower reaction temperature the range of by-products that are formed are limited. Under these conditions the 2.5 wt.% Au–2.5 wt.% Pd/TiO_2 was found to be the most active catalyst, whereas the Au/TiO_2 catalyst demonstrated the highest selectivity to benzaldehyde. Toluene, formed *via* either a hydrogen transfer process or an oxygen transfer process, was observed as a major by-product under these forcing conditions.

Keywords: Benzyl alcohol oxidation; Gold; Palladium; Titania

1. Introduction

The oxidation of alcohols to acids and aldehydes using gold catalysts has been one of the success stories of gold catalysis, following the seminal studies of Rossi and Prati [1–7]. In the early studies gold in nano-crystalline form was shown to catalyze alcohols and diols to acids in the presence of base. Subsequently, these studies were extended to show that glycerol, a bio-renewable feedstock, could be oxidized in high specificity to glycerate [8,9]. Rossi and co-workers demonstrated that supported gold catalysts could oxidise alcohols to aldehydes using gas phase reactants and products [10]. In a seminal study, Corma and co-workers have shown that Au/CeO_2, especially when using nanocrystalline CeO_2, is particularly effective for the oxidation of alcohols selectively to the corresponding aldehyde [11]. They based this discovery on the observation that these Au/CeO_2 catalysts generated a peroxy species from molecular oxygen using *in situ* infrared spectroscopy, and they noted that as this species can be selective in alcohol oxidation then the Au/CeO_2 catalysts should be effective for this reaction. This was indeed the case and these Au/CeO_2 catalysts were clearly demonstrated to be more active than the best supported Pd catalysts available at that time [12]. Subsequently, Corma and co-workers also showed [13] that this catalyst was extremely effective for the oxidation of aldehydes to acids and also the oxidation of allylic alcohols [14] for which this catalyst had a particular efficacy for the selective transformation. At much the same time we were working on the design of catalysts for the selective oxidation of hydrogen with molecular oxygen for the direct synthesis of hydrogen peroxide [15–19]. Using a similar logic to that expressed by Corma and co-workers [11] we considered that catalysts effective for the direct synthesis of hydrogen peroxide should be equally effective for the selective oxidation of alcohols. Subsequently, we demonstrated [20,21] very high activity and selectivity could be obtained using Au–Pd/TiO_2 or Au/TiO_2 catalysts when tested under mild solvent free conditions. In particular, this 2.5 wt.% Au–2.5 wt.% Pd/TiO_2 catalyst was over 25 times more active for the selective oxidation of phenylethanol when compared with the Au/CeO_2 [11] or Pd/hydroxyapatite [12] catalysts under the same reaction conditions [20].

In this short paper we add to our earlier study of the Au–Pd/TiO_2 catalyst and examine the effect of the Au–Pd ratio on the

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catalyst performance, and in particular on the formation of non-selective reaction products using the oxidation of benzyl alcohol as a model reaction.

2. Experimental

2.1. Catalyst preparation

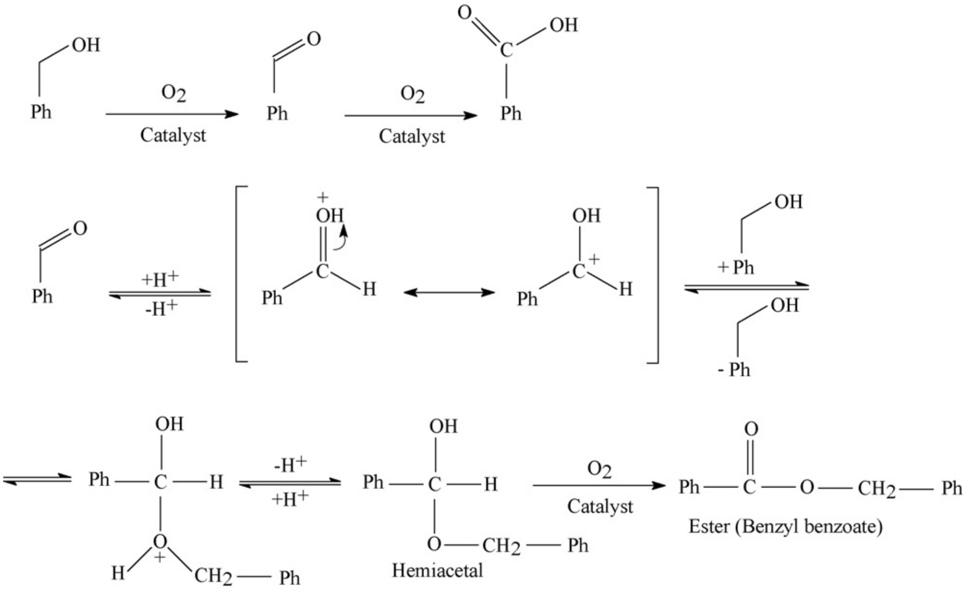
The 5 wt.% Pd/TiO_2, 5 wt.% Au/TiO_2 and a range of Au–Pd/TiO_2 catalysts were prepared by impregnation of (Degussa P25, mainly anatase) *via* an incipient wetness method using aqueous solutions of $PdCl_2$ (Johnson Matthey) and/or $HAuCl_4{\cdot}3H_2O$ (Johnson Matthey). For the 2.5% Au–2.5% Pd/TiO_2 catalyst the detailed procedure was as follows. The 10 ml of an aqueous solution of $HAuCl_4{\cdot}3H_2O$ (5 g in 250 ml of water) and 4.15 ml of an aqueous $PdCl_2$ solution (1 g in 25 ml of water) were simultaneously added to TiO_2 (3.8 g). The paste formed was ground and dried at 80 °C for 16 h and finally calcined in static air at 400 °C for 3 h. Catalyst with other Au:Pd ratios were prepared in a similar manner using the appropriate concentrations of the gold and palladium salts. Au, Pd and Au–Pd supported catalysts prepared by this methodology have been extensively characterized in our previous studies [15–20]. In particular the Au–Pd/TiO_2 catalysts, as typified by the 2.5% Au–2.5% Pd/TiO_2 catalyst, exhibit a core-shell morphology with a gold rich core and a palladium rich surface, but all the particles are Au–Pd alloys [20].

2.2. Catalyst testing

The oxidation of benzyl alcohol oxidation was carried out in a stirred reactor (100 ml, Autoclave Engineers Inline MagneDrive III). The vessel was charged with alcohol (40 ml) and catalyst (0.007 g unless otherwise specified). The autoclave was then purged five times with oxygen before setting the initial reaction pressure of O_2 at 10 bar gauge. Concerning the start-up procedure, this was carried out with the oxygen line opened, and as the oxygen was consumed it was replaced from the cylinder, maintaining the overall pressure constant. The stirrer was a down-flow turbine, that ensures the gas and the liquid are thoroughly mixed. The stirrer was set at 1500 rpm and the reaction mixture was raised to the required temperature. The effects of mass transfer limitation were evaluated in detail to ensure no effects of mass transfer limitation were present. At 160 °C the reaction became mass transfer limited with catalyst masses over 25 mg under these conditions, whereas at 100 °C the reaction only became mass transfer limited when catalyst masses of ca. 200 mg were utilized. Hence the use of very low catalyst mass (7 mg) ensures the absence of mass transfer limitation under our reaction conditions. Samples from the reactor were taken periodically, *via* a sampling system, ensuring that the volume purged before sampling was higher than the tube volume. For the identification and analysis of the products a GC–MS and GC (equipped with a capillary column, DB-Wax column), were used and checked by comparison with authentic samples.

3. Results and discussion

In a previous detailed paper [17] we have shown that the 2.5 wt.%–2.5 wt.% Pd/TiO_2 catalyst was very effective for the oxidation of a range of alcohol, including benzyl alcohol, to the corresponding aldehydes. In particular, we showed that under mild solvent free conditions (100 °C, 2 bar O_2, 0.2 g catalyst) complete conversion could be achieved over a few hours reaction time giving a yield of benzaldehyde around 90%. Under these conditions a range of by-products was formed, including the ester and acetal products. The mechanisms by which these products are formed are shown in Schemes 1 and 2. We also showed [20] that most of the by-products could also be oxidised to benzaldehyde under these conditions. However, under these mild conditions the amounts of the individual by-



Scheme 1.