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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

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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

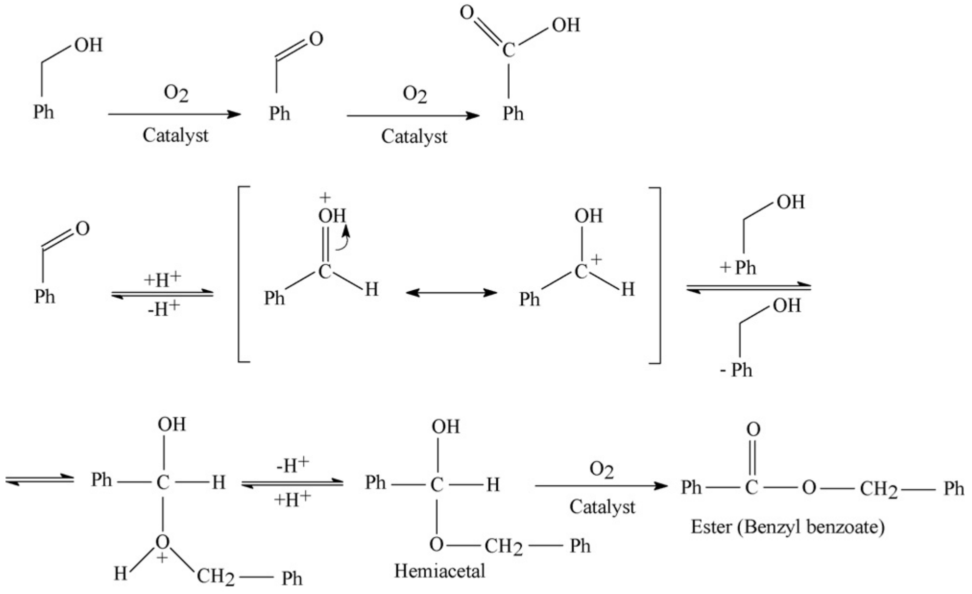
The 5 wt.% Pd/TiO_2, 5 wt.% Au/TiO_2 and a range of Au–Pd/TiO_2 catalysts were prepared by impregnation of (Degussa P25, mainly anatase) *via* an incipient wetness method using aqueous solutions of $PdCl_2$ (Johnson Matthey) and/or $HAuCl_4 \cdot 3H_2O$ (Johnson Matthey). For the 2.5% Au–2.5% Pd/TiO_2 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

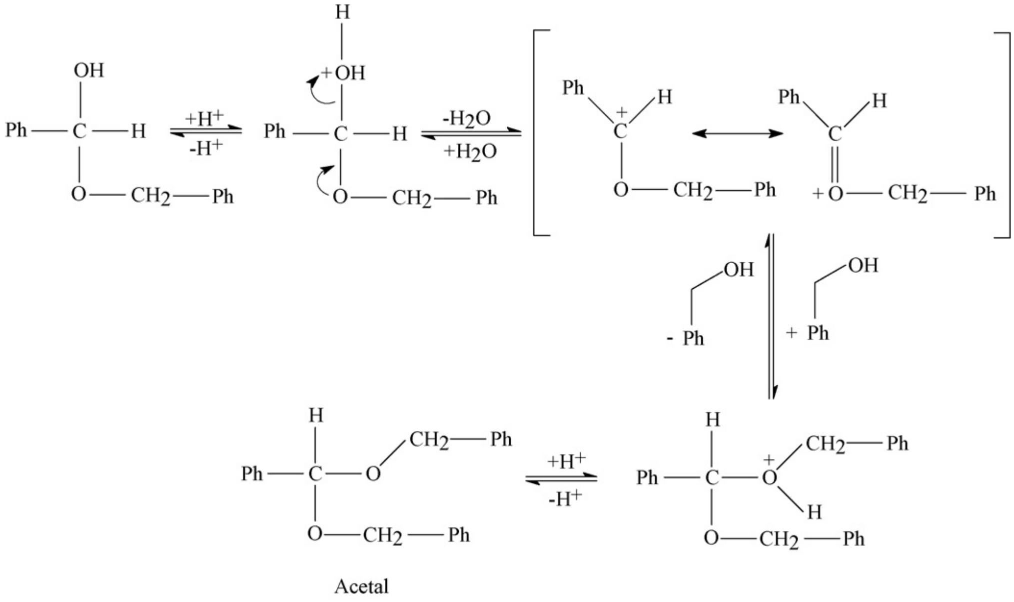
The oxidation of benzyl alcohol oxidation was carried out in a stirred reactor (100 ml, Autoclave Engineers Inline MagneDrive III). The vessel was charged with alcohol (40 ml) and catalyst (0.007 g unless otherwise specified). The autoclave was then purged five times with oxygen before setting the initial 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.



Scheme 2.

products is very small. We wished to study the formation of the by-products and, in particular, the effect of the Au:Pd ratio on by-product formation. For this reason we have used more forcing reaction conditions (160 °C, 10 bar O_2, 0.007 g catalyst) to enable the formation of by-products to be observed.

Our initial experiments were conducted to determine the effect of the Au:Pd ratio on catalyst activity for this reaction and the results are shown in Table 1. These are contrasted with data obtained by making physical mixtures of the Au/TiO_2 and Pd/TiO_2 catalysts to give the corresponding amounts of Au and Pd. From this it can be seen that the addition of Au to Pd for the alloy catalysts gives significant differences from the linear trend expected from the physical mixtures. The catalyst with the best compromise between activity and selectivity comprises 2.5 wt.% Au–2.5 wt.% Pd/TiO_2. This is also in agreement with the activity of these catalysts for hydrogen peroxide synthesis which is also at a maximum for this formulation as compared with 5 wt.% Au/TiO_2 and 5 wt.% Pd/TiO_2 catalysts.

Our main purpose was to contrast the effect of the Au:Pd ratio on the selectivity for the reaction and this we have achieved by plotting selectivity versus benzyl alcohol conversion, at the constant reaction temperature of 160 °C. At this elevated temperature and with excess oxygen present, the selectivity to the main product of benzaldehyde (Fig. 1) is significantly lower than that observed at 100 °C of >90% for the 2.5 wt.% Au–2.5 wt.% Pd/TiO_2 catalyst [20]. A full set of data obtained for these catalysts at 100 °C is shown in Table 2 as a means of comparison. We observed the highest selectivity with the Au/TiO_2 catalyst and the addition of Pd decreased this gradually, but at high conversions the selectivity to benzaldehyde under these forcing conditions was low. This was due to the formation of two major by-products which are observed at high benzyl alcohol conversion. First, the over-oxidation to benzoic acid is, as expected, a facile process at 160 °C (Fig. 2) and general the conversion of benzaldehyde to benzoic acid does not require the intervention of a catalyst. Clearly, to achieve high selectivities this process has to be limited at high

Table 1
Effect of the Au:Pd ratio on the oxidation of benzyl alcohol at 160 °C

Catalyst	TOF (h^{-1})[a]	
	Au–Pd catalysts	Au–Pd physical mixtures
5% Au/TiO_2	33,700	33,700
4% Au–1% Pd/TiO_2	47,600	42,300
3% Au–2% Pd/TiO_2	48,700	50,800
2.5% Au–2.5% Pd/TiO_2	65,400	55,100
2% Au–3% Pd/TiO_2	65,100	59,400
1% Au–4% Pd/TiO_2	64,000	67,900
5% Pd/TiO_2	76,500	76,500

[a] Determined at 0.5 h reaction time.

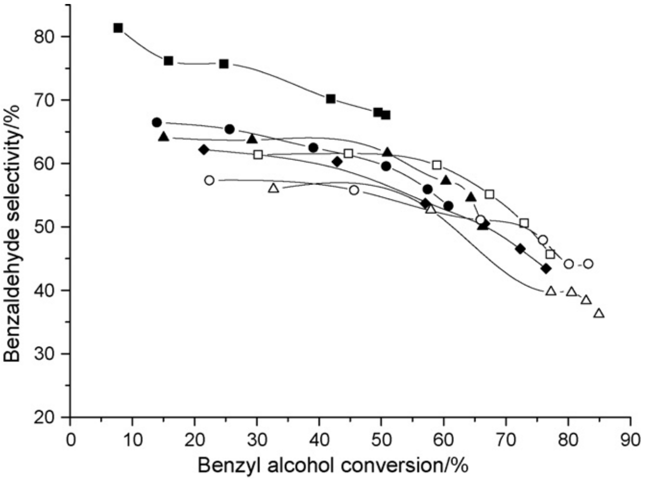


Fig. 1. Selectivity to benzaldehyde as a function of benzyl alcohol conversion (160 °C, 10 bar O_2, 0.007 g catalyst); (■) 5% Au/TiO_2; (●) 4% Au–1% Pd/TiO_2; (▲) 3% Au–2% Pd/TiO_2; (◆) 2.5% Au–2.5% Pd/TiO_2; (□) 2% Au–3% Pd/TiO_2; (○) 1% Au–4% Pd/TiO_2; (△) 5% Pd/TiO_2.

Table 2
Effect of the Au:Pd ratio on the oxidation of benzyl alcohol at 100 °C[a]

	Catalyst									
	5% Au/TiO_2		4% Au–1% Pd/TiO_2		2.5% Au–2.5% Pd/TiO_2		1% Au–4% Pd/TiO_2		5% Pd/TiO_2	
Time on line (h)	0.5	1.0	0.5	1.0	0.5	1.0	0.5	1.0	0.5	1.0
Conversion (%)	0.1	0.2	1.0	1.9	1.9	3.4	1.0	2.3	1.2	2.5
Selectivity (%)										
Benzaldehyde	100	95.0	94.0	91.3	82.8	85.6	80.6	79.1	65.6	69.8
Benzoic acid	–	2.3	1.3	1.8	3.1	1.2	1.8	1.1	0.7	1.2
Toluene	–	2.6	2.5	3.5	5.6	7.0	7.7	13.8	21.7	20.5
Benzyl benzoate	–	–	2.2	3.2	8.5	6.2	5.0	3.9	4.4	5.7

[a] Reaction conditions: 100 °C, 0.1 g catalyst, 40 ml benzyl alcohol, PO_2 10 bar.

conversion and this is effected by using lower O_2 partial pressure and temperature combined with a higher catalyst mass to ensure rapid catalysis of the primary catalysed pathway [20]. The second by-product was more surprising in that toluene was observed in very high selectivities particularly with the Pd-rich catalysts (Fig. 3). This pathway occurs in the absence of O_2 and we demonstrated this in a subsequent reaction where benzyl alcohol (40 ml) was stirred with the 2.5 wt.% Au–2.5 wt.% Pd/TiO_2 catalyst at 160 °C in the presence of He in place of O_2 and initially toluene and benzaldehyde were formed in equimolar amounts (Scheme 3) *via* either a hydrogen transfer process or an oxygen transfer process mediated by Pd. This is possibly catalysed by the Pd-rich surfaces of the catalysts since with the Au only catalyst the formation of toluene is minimised but it is not totally eradicated (Fig. 3). As noted earlier (Table 2) toluene is formed at short reaction times when the reaction temperature is 100 °C and its formation increases with the amount of Pd in the catalyst formulation. We find that toluene is formed in the mixed Au–Pd/TiO_2 catalysts even at very low conversions and at short reaction times, indicating it is possibly a primary reaction product. Recently, Corma and co-workers [11,14] has shown spectroscopically that Au–H and Pd–H species are formed on supported Au and Pd catalysts, and these can be expected to be important in the formation of toluene in the present system.

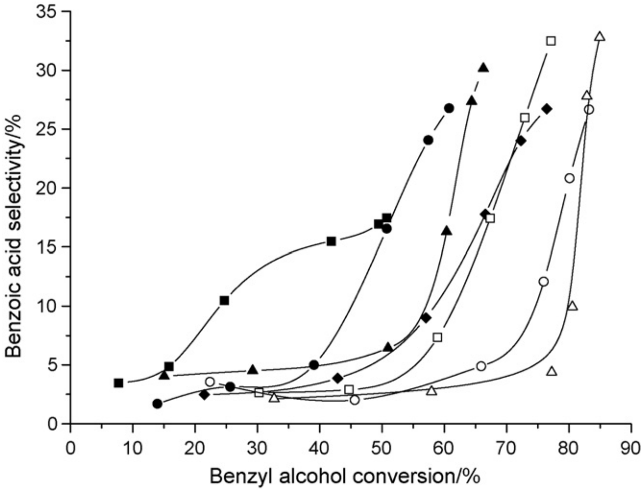


Fig. 2. Selectivity to benzoic acid as a function of benzyl alcohol conversion (160 °C, 10 bar O_2, 0.007 g catalyst); (■) 5% Au/TiO_2; (●) 4% Au–1% Pd/TiO_2; (▲) 3% Au–2% Pd/TiO_2; (◆) 2.5 % Au–2.5% Pd/TiO_2; (□) 2% Au–3% Pd/TiO_2; (○) 1% Au–4% Pd/TiO_2; (△) 5% Pd/TiO_2.

The selectivities to benzyl benzoate and benzyl acetyl were much lower (Figs. 4 and 5). The selectivity to the acetal decreased with conversion demonstrating that it was being converted to other products, including benzaldehyde.

The observation, under these forcing reaction conditions that toluene can be a major production was unexpected. It is formed

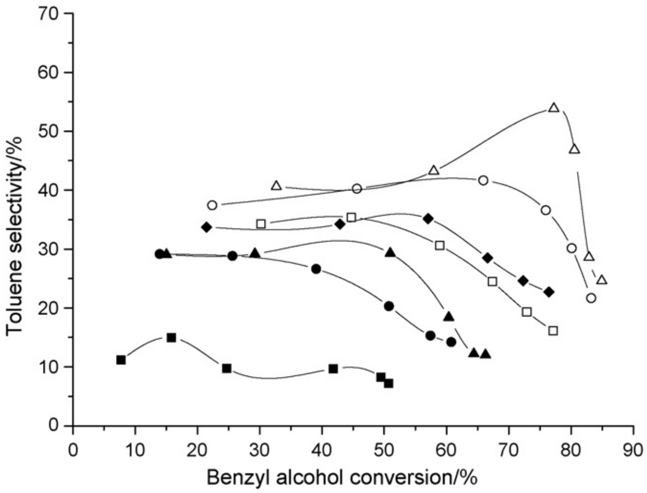
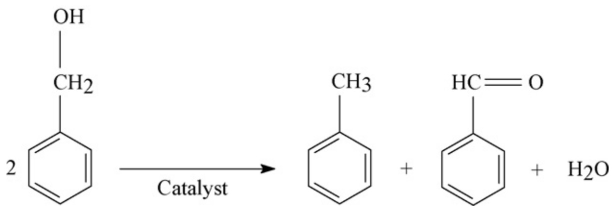


Fig. 3. Selectivity to toluene as a function of benzyl alcohol conversion (160 °C, 10 bar O_2, 0.007 g catalyst); (■) 5% Au/TiO_2; (●) 4% Au–1% Pd/TiO_2; (▲) 3% Au–2% Pd/TiO_2; (◆) 2.5% Au–2.5% Pd/TiO_2; (□) 2% Au–3% Pd/TiO_2; (○) 1% Au–4% Pd/TiO_2; (△) 5% Pd/TiO_2.



Scheme 3.

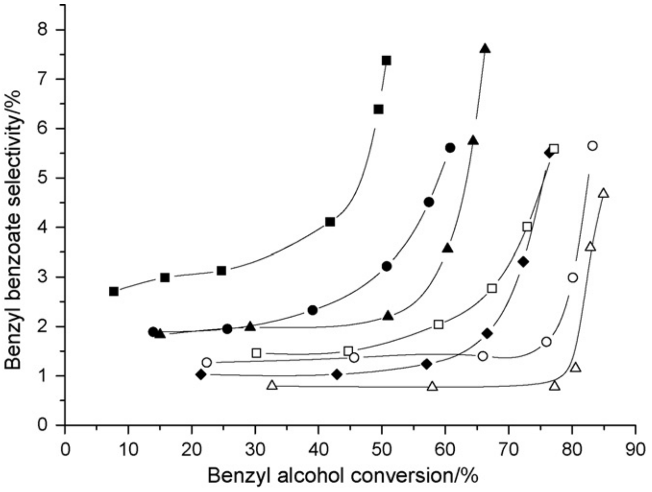


Fig. 4. Selectivity to benzyl benzoate as a function of benzyl alcohol conversion (160 °C, 10 bar O_2, 0.007 g catalyst); (■) 5% Au/TiO_2; (●) 4% Au–1% Pd/TiO_2; (▲) 3% Au–2% Pd/TiO_2; (◆) 2.5% Au–2.5% Pd/TiO_2; (□) 2% Au–3% Pd/TiO_2; (○) 1% Au–4% Pd/TiO_2; (△) 5% Pd/TiO_2.

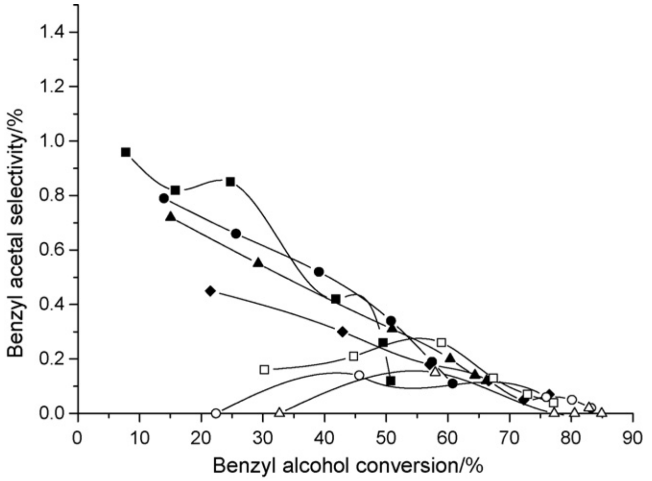


Fig. 5. Selectivity to benzyl acetyl as a function of benzyl alcohol conversion (160 °C, 10 bar O_2, 0.007 g catalyst); (■) 5% Au/TiO_2; (●) 4% Au–1% Pd/TiO_2; (▲) 3% Au–2% Pd/TiO_2; (◆) 2.5% Au–2.5% Pd/TiO_2; (□) 2% Au–3% Pd/TiO_2; (○) 1% Au–4% Pd/TiO_2; (△) 5% Pd/TiO_2.

in very small amounts under mild conditions (100 °C). The observation of this reaction product opens up a number of further reactions possibilities for Au–Pd catalyst and this is a topic worthy of further investigation.

Acknowledgements

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