

# Activity of Catalysts Derived from Au<sub>101</sub> Immobilized on Activated Carbon

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Abstract The performance of catalysts made using Au<sub>101</sub>(PPh<sub>3</sub>)<sub>21</sub>Cl<sub>5</sub> nanoparticles immobilized on Norit<sup>®</sup> activated carbon powder was investigated in the aerobic oxidation of benzyl alcohol in basic methanolic solution. The catalyst was activated by washing with hot toluene, followed by heat treatment in static air at 100 °C for 3 h. Effects of key parameters, such as the amounts of benzyl alcohol and base (K<sub>2</sub>CO<sub>3</sub>), reaction temperature, reaction time and solvent were explored, as was the longer-term stability of the catalyst during storage. The product mixtures were analysed by high-performance liquid chromatography. Under relatively mild conditions  $[p(O_2) = 5 \text{ bar} \text{ and}$ T = 80 °C], catalysts with a loading of 1.0 wt% give up to 100 % conversion of benzyl alcohol in the presence of equimolar K<sub>2</sub>CO<sub>3</sub> over 24 h. The main products are methyl benzoate and benzoic acid, with selectivities that vary with reaction conditions. Comparison with results obtained with ethanol solvent support a reaction mechanism involving benzaldehyde as an intermediate.

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# 1 Introduction

Gold nanoparticles exhibit remarkable catalytic properties and genuine "nanosize" effects, which were discovered in the 1970s [1], but not exploited until the late 1980s [2]. Gold-containing materials derived from triphenylphosphine-(PPh<sub>3</sub>) stabilized clusters, ranging from Au<sub>9</sub> (PPh<sub>3</sub>)<sub>8</sub>(NO<sub>3</sub>)<sub>3</sub> to Au<sub>101</sub>(PPh<sub>3</sub>)<sub>21</sub>Cl<sub>5</sub> (hereafter abbreviated as Au<sub>101</sub>), have been shown to be active catalysts for oxidation of organic compounds [3–5]. The PPh<sub>3</sub> ligands play a deactivating role by shielding the gold cores [6], but can be removed by thermal treatments, thereby facilitating catalytic activity [3]. However, comprehensive and systematic studies of the effects of reaction parameters in these types of catalysts are relatively scarce [7, 8].

Although there are reports of the use of such catalysts in base-free benzyl alcohol oxidation in the literature [9], the majority rely on the use of base to achieve high conversions under mild conditions [10, 11]. In 2011, Prati et al., highlighted that "...selectivity of the reaction can be strongly affected by the presence of a base, whose function is still under investigation" [9]. In regards to the catalytic oxidation of benzyl alcohol by immobilized Au nanoparticles in the presence of a base: Zhu et al., found that the use of base as well as the type of base played a key role in the activity of Au particles immobilized on activated carbon for benzyl alcohol oxidation in toluene [12], Dimitratos et al. reported 48 % conversion over 6 h at 160 °C under solvent free conditions using Au immobilized on carbon [13]. In comparison, Isida and co-workers achieved better than 99 % oxidation of benzyl alcohol by Au particles immobilized on activated carbon in the presence of K<sub>2</sub>CO<sub>3</sub> over 1 h at 80 °C, in striking contrast to just 12 % conversion over 3 h under the same conditions without base [14]. Finally, recent, topical investigations focused on studies of Au nanoparticles immobilized on custom-made, high-surface-area carbonaceous supports as catalysts in benzyl alcohol oxidation, utilized base to facilitate reaction [15, 16].

This paper focusses on the effects of systematic alterations of the reaction conditions on the activity and selectivity of catalysts made using  $Au_{101}$  as a precursor, deposited and activated on commercially available activated carbon (Norit<sup>®</sup>) designed specifically for the fabrication of catalysts, in the aerobic oxidation of benzyl alcohol in the presence of K<sub>2</sub>CO<sub>3</sub>.

### **2** Experimental Section

Au<sub>101</sub> was synthesized according to the method of Weare et al. [17], and its identity was confirmed by <sup>1</sup>H NMR in CDCl<sub>3</sub>. The supported gold catalyst, hereafter designated 1.0 wt% Au<sub>101</sub>/ AC, was fabricated by stirring (750 rpm) ~5 g of Norit<sup>®</sup> SX1G activated carbon powder (Cabot Corporation; BET surface area of *ca*. 800 m<sup>2</sup>/g) with ~50 mg of Au<sub>101</sub> in 200 mL of dichloromethane until the solvent became colourless (~2 h), indicating (near-) complete deposition of nanoparticles on to the support. The product was centrifuged, washed several times with CH<sub>2</sub>Cl<sub>2</sub>, dried under vacuum for a day, washed in hot toluene then heated in static air at 100 °C for 3 h following a protocol described by Lopez-Sanchez et al. [18]. Catalyst that was not used immediately was stored under N<sub>2</sub> and in the dark at -4 °C.

High-resolution transmission electron microscopy (TEM) was performed using a Philips CM20 operating at 200 kV in bright-field mode. Samples for TEM study were

prepared by ultrasonically dispersing the relevant material in methanol, depositing a drop of the suspension onto holey carbon-film-coated 300-mesh copper grid and then allowing the solvent to evaporate under vacuum for  $\sim 2$  h. Particle diameter distributions were determined by using *ImageJ* open-source software to measure and count at least 100 particles in high magnification micrographs.

Oxidation reactions were carried out in a 50-mL stainless-steel pressurized batch reactor. The Teflon reactor liner was charged with 1.25 mmol anisole (internal chromatography standard), 50 mg of 1.0 wt% Au<sub>101</sub>/AC, up to 2.5 mmol benzyl alcohol (reactant), up to 2.5 mmol of K<sub>2</sub>CO<sub>3</sub> and a magnetic stirring bar, and then made up a volume of 25 mL with methanol. The reactor was purged five times, pressurised to  $5.03 \pm 0.07$  bar with oxygen and then heated on a magnetic stirring (750 rpm) hotplate over  $\sim 20$  min to the target temperature  $\pm 2$  °C. After the desired reaction period, the reactor was cooled in ice for  $\sim 1$  h to ensure that volatiles had condensed, after which the remaining gas was vented. The catalyst was separated by centrifugation (5000 rpm, 15 min) and the product mixtures were analysed using a Dionex high-performance liquid chromatography (HPLC) system fitted with a Luna 5 µ C18 reverse-phase column and a UV detector. The conversion (C) and selectivity (S) were calculated as:

$$C = \left[ (n_{\text{react}})_{i} - (n_{\text{react}})_{f} \right] / (n_{\text{react}})_{i} \times 100 \%$$
  

$$S_{\text{prod}} = \left( n_{\text{prod}} \right)_{f} / \left[ (n_{\text{react}})_{i} - (n_{\text{react}})_{f} \right] \times 100 \%$$

where  $n_{\text{react}}$  and  $n_{\text{prod}}$  represent the molar amounts of reactants and products and the subscripts i and f indicate the initial and final states of the reaction, respectively. Each experiment was repeated at least three times in order to ensure reproducibility.

#### **3** Results and Discussion

TEM images and size-distribution data for "as-synthesized" Au<sub>101</sub> (Fig. 1a) indicate a mean particle diameter of 1.64  $\pm$  0.05 nm (uncertainty is two standard errors of the mean), including about 11 % with diameters greater than 2 nm [5]. This is just slightly larger than the core diameter of 1.5  $\pm$  0.5 nm determined for the precursor Au<sub>101</sub> particles [17]. After immobilization, the mean diameter of the gold-containing particles increased to 2.62  $\pm$  0.12 nm (Fig. 1b), the standard deviation of the distribution nearly doubled and only ~16 % of the particles had diameters less than 2 nm. These indications of particle aggregation are consistent with observations where deposition of Au<sub>101</sub> onto oxides resulted in particle size increases to 2.0–2.7 nm (depending on loading) for Au<sub>101</sub>/TiO<sub>2</sub> [19] and ~2.2 nm for Au<sub>101</sub>/WO<sub>3</sub> [20]. However, on SiO<sub>2</sub>,



**Fig. 1** TEM images and particle diameter frequency histograms of: **a** untreated "as-synthesized" Au<sub>101</sub>; **b** 1.0 wt% Au<sub>101</sub>/AC after immobilisation but before activation; **c** 1.0 wt% Au<sub>101</sub>/AC after activation by washing with hot toluene and heating in static air at

Au<sub>101</sub> particles appear less prone to aggregation ( $\sim 1.6$  nm for 0.1 wt% Au<sub>101</sub>/SiO<sub>2</sub>) [5].

Washing with toluene followed by heat treatment caused a 16 % additional increase of the mean diameter to  $3.05 \pm 0.07$  nm (Fig. 1c), but sharpened the distribution by about 25 %. In XPS studies of Au clusters (including  $Au_{101}$ ) on TiO<sub>2</sub>, we demonstrated a similar trend upon washing in hot toluene [21]. Similarly, Dimitratos et al. observed a significant increase in the particle size upon heating in air at 250 °C from 3.5  $\pm$  1.6 to 8.7  $\pm$  5.2 nm for 1 wt% Au/C prepared by sol immobilization [13]. Storage for up to 6 months (Fig. 1d) caused no significant further change in the average size, but the distribution became more than 50 % broader, with about one in eight particles having diameters greater than 4 nm. Zanella and Louis have demonstrated that storage can lead to a detrimental increase in particle size for Au supported on TiO<sub>2</sub>, which they attributed to water [22], while DiCenzo et al. estimated that Au<sub>n</sub> clusters on carbon support transition from non-metallic to metallic behaviour with *n* greater than ca. 150 [23]. On this basis, we conclude that the particles in this work are predominantly metallic, albeit with sizes at the lower boundary of the metallic regime.

Table 1 demonstrates the important role of base  $(K_2CO_3)$  in the Au<sub>101</sub>/AC-catalysed oxidation of benzyl

100 °C for 3 h; **d** activated 1.0 wt% Au<sub>101</sub>/AC after 6 months of storage in the dark at -4 °C. The mean particle diameters (in nm with uncertainties of two standard deviations of the mean) and standard deviations of the distributions (nm) are indicated

alcohol. In accord with previous observations [14], conversion is dependent on the presence and concentration of base. No conversion occurs over 24 h at 80 °C in the absence of base, rising to 100 % under the same conditions with a 1:1 mol ratio of benzyl alcohol to  $K_2CO_3$ . The selectivities are dependent on the specific concentrations. A mixture of 2.5:2.5 mmol gives 100 % conversion with selectivity strongly favouring ( $\sim 78$  %) methyl benzoate. Halving the amount of K<sub>2</sub>CO<sub>3</sub> decreases conversion to 33 %, with the selectivity in favour of methyl benzoate reduced to ~66 % and with a small amount (~3 %) of benzaldehyde produced. Subsequently decreasing the benzyl alcohol to give an equimolar 1.25:1.25 mmol ratio restores 100 % conversion, but now with nearly equal proportions of benzoic acid and methyl benzoate (and no detectable benzaldehyde). When the base concentration is increased to twice that of benzyl alcohol, conversion is just 51 %, with benzoic acid now the main product ( $\sim$ 76 %) and a small amount ( $\sim 2\%$ ) of benzaldehyde. Better selectivity for methyl benzoate is achieved with higher, equimolar concentrations of reactant and base, whereas better selectivity for benzoic acid is achieved with excess base, albeit at the expense of lower conversion. These differences point to different base dependence of the reaction channel kinetics for these two products.

Table 1 Conversion (C) and selectivities (S) of the oxidation of benzyl alcohol in the presence of activated 1.0 wt% Au<sub>101</sub>/AC as a function of the ratio (mmol:mmol) of benzyl alcohol to K<sub>2</sub>CO<sub>3</sub>

Benzyl alcohol:K <sub>2</sub> CO <sub>3</sub> (mmol:mmol)	С %	S %			
		Benzoic acid	Methyl benzoate	Benzaldehyde	
2.5:2.5	100	22	78	0	
2.5:1.25	33	29	66	3	
1.25:1.25	100	47	53	0	
1.25:2.5	51	76	21	2	

Reactions were performed for 24 h at 80 °C with methanol as the solvent



Fig. 2 Conversion (C) and selectivities (S) of the catalytic oxidation of benzyl alcohol by activated 1.0 wt% Au<sub>101</sub>/AC in methanol as a function of reaction temperature. Reactions were performed for 24 h with a starting benzyl alcohol to K<sub>2</sub>CO<sub>3</sub> ratio of 2.5:2.5 mmol. The dashed curves are intended merely to guide the eye

Figure 2 shows conversion and selectivities after 24 h as functions of temperature up to 100 °C with an initial benzyl alcohol-to-base ratio of 2.5:2.5 mmol, which gives the greatest selectivity towards methyl benzoate. Below ~40 °C, conversion is less than 10 %; it then increases dramatically to  $\sim 86$  % at 60 °C and saturates near 100 % above ~80 °C. At lower temperatures, methyl benzoate production is strongly favoured, which is consistent with earlier observations at mild temperatures [8, 14], and a small amount ( $\sim 2$  %) of benzaldehyde is produced.

Figure 3 shows the conversion and selectivities for aerobic oxidation of benzyl alcohol at 80 °C as a function of time with an initial benzyl alcohol to K<sub>2</sub>CO<sub>3</sub> ratio of 2.5:2.5 mmol. After an induction period of  $\sim 1$  h, conversion increases abruptly to  $\sim 75$  % after 3 h,  $\sim 96$  % after 6 h and 100 % after 12 h. The main product is methyl benzoate, with benzaldehyde as a minor product ( $\sim 2\%$ ) until  $\sim 3$  h reaction time, at which point it could be detected only in trace amounts. Immediately after induction, the ratio of methyl benzoate to benzoic acid is as high as  $\sim 9.1$ , but decreases monotonically to  $\sim 2.3:1$  after 6 h, then more gradually to an apparent asymptote of  $\sim 2:1$  near 24 h.

A common problem with gold catalysts is a difference in results obtained using freshly made and stored catalysts [22]. The TEM data above suggest that the catalyst used in



Fig. 3 Conversion (C) and selectivities (S) of the catalytic oxidation of benzyl alcohol by activated 1.0 wt% Au<sub>101</sub>/AC in methanol as a function of reaction time. Reactions were performed at 80 °C with a starting benzyl alcohol to K<sub>2</sub>CO<sub>3</sub> ratio of 2.5:2.5 mmol. The dashed curves are intended merely to guide the eye

this work is sufficiently stable against aggregation to avoid deactivation during storage in the dark under  $N_2$  at -4 °C for up to six months. Indeed, aerobic oxidation over 3 h (with all other parameters as described for Fig. 3) with freshly prepared or stored catalyst gave essentially identical results (Table 2). The reaction time of 3 h was used to ensure that any differences in performance would not be obscured by the reactions saturating at 100 % conversion.

We now turn to the mechanism of the reaction. It has been suggested [11] that this involves benzaldehyde as an intermediate, followed by oxidization to benzoic acid [14] or oxidative esterification involving the solvent [11] (Scheme 1), which is consistent with the production of small amounts of benzaldehyde in low-conversion reactions (Table 1; Figs. 1 and 2). If correct, a change from methanol to ethanol should produce ethyl benzoate [24]. Indeed, with ethanol, benzoic acid and ethyl benzoate are produced (Table 3), but with much reduced conversion and selectivities, and substantial amounts of other materials, which are possibly products of oxidative self-esterification of the solvent. With toluene as a solvent, no conversion is achieved.

Finally, we compare our results with other recent related studies. In general terms, we find that our  $\sim 3$  nm particles **Table 2** The effect of 6 months storage at -4 °C on the performance of activated 1.0 wt% Au<sub>101</sub>/AC in catalytic oxidation of benzyl alcohol in methanol

Au <sub>101</sub> /AC	С %	S %			
		Benzaldehyde	Benzoic acid	Methyl benzoate	
Fresh	$76 \pm 2$	0	$22 \pm 1$	$78 \pm 1$	
Stored	$74 \pm 1$	0	$26 \pm 1$	$74 \pm 2$	

Reactions were performed for 3 h at 80 °C with a starting benzyl alcohol to K2CO3 ratio of 2.5:2.5 mmol

Scheme 1 Reaction pathway of benzyl alcohol oxidation in the presence of the base and methanol by activated 1.0 wt% activated Au<sub>101</sub>/AC catalysts



Table 3 The effect of solvent on oxidation of benzyl alcohol using activated 1.0 wt%  $Au_{101}/AC$ 

Solvent	С %	S %					
		Benzaldehyde	Benzoic acid	Methyl benzoate	Ethyl benzoate	Others	
Methanol	100	0	22	78	0	0	
Ethanol	34	1	8	0	11	80	
Toluene	0	0	0	0	0	0	

Reactions were performed for 24 h at 80 °C with a starting benzyl alcohol to K<sub>2</sub>CO<sub>3</sub> ratio of 2.5:2.5 mmol

in basic methanolic solution give predominantly methyl benzoate and benzoic acid, with the benzaldehyde observed only at short reaction times and lower temperatures. This is in contrast to findings by Prati et al. for  $\sim 3$  nm Au particles supported on carbon nanofibres under base-free aqueous (pH 8.2-8.5) conditions at 60 °C, where selectivity for benzaldehyde was ~90 % even at ~90 % conversion [9]. Of course, methyl benzoate is not an expected product in the absence of methanol, but it is interesting to note that their reaction did not proceed efficiently to benzoic acid. More recently, Tsukuda et al. studied of benzyl-alcohol oxidation in basic aqueous solution at 30 °C by Au/C catalysts derived from thiol-protected Au<sub>25</sub> clusters activated under various temperatures under vacuum [15]. They concluded that the fully ligated clusters are inactive, but are activated by ligand removal. At low levels of ligand removal they reported selectivity in favour of benzaldehyde, while complete removal resulted in greater catalytic activity and switched selectivity to benzoic acid. This would appear to suggest that it is the absence of base, rather than the nature of water as a solvent, that leads to benzaldehyde as the major product, as found by Prati et al. Finally, a very recent report by Wang et al. shows that, in aqueous base (KOH) at 60 °C,  $\sim 3$  nm Au nanoparticles supported on mesoporous carbon show high activity with selectivity towards benzoic acid, with only minimal amounts of benzaldehyde and benzyl benzoate observed at low conversions [16]. All of these observation point to the importance of base to progress oxidation through to the acid product in Scheme 1. Clearly, in our case, it is the huge excess of methanol used as a solvent that facilitates formation of methyl benzoate in competition with the benzoic acid branch of the reaction scheme.

## 4 Conclusions

This study showed that activated 1.0 wt%  $Au_{101}/AC$  is an effective catalyst for aerobic oxidation of benzyl alcohol in basic methanolic solution under relatively mild conditions. Selectivity can be tuned towards methyl benzoate or benzoic acid, depending on the exact choice of conditions

(e.g., the ratio of benzyl alcohol to base and reaction temperature). The catalyst shows high conversion, as well as good long-term retention of activity on storage. The results support a reaction mechanism whereby benzyl alcohol is initially oxidized to benzaldehyde, which then undergoes further oxidation to benzoic acid or oxidative esterification to methyl benzoate. The involvement of the solvent is bolstered by the observation that its change to ethanol produces ethyl benzoate, albeit in lower yield. This catalyst appears to be a promising candidate for sustainable processes using simple and relatively environmentally benign reagents, including  $O_2$ .

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- S. Ghadamgahi et al.
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