Available online at www.sciencedirect.com
ScienceDirect
Catalysis Today 122 (2007) 317–324
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Solvent free liquid phase oxidation of benzyl alcohol using Au supported catalysts prepared using a sol immobilization technique

Nikolaos Dimitratos [a], Jose Antonio Lopez-Sanchez [a], David Morgan [a], Albert Carley [a], Laura Prati [b], Graham J. Hutchings [a,*]

[a] *School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, UK*
[b] *Dipartimento di Chimica Inorganica Metallorganica e Analitica e ISTM, Centre of Excellence CIMAINA, Università di Milano, via Venezian 21, I-20133 Milano, Italy*

Abstract

Solvent free oxidation of benzyl alcohol was investigated in the absence of a base using Au catalysts prepared by sol immobilization on titania and carbon supports. Comparison between the Au supported catalysts revealed that activity and distribution of products was dependent on the nature of support and heat treatment. Specifically, heat pre-treatment of the Au catalysts has a beneficial effect in terms of activity, but is detrimental in terms of selectivity to the benzaldehyde. We conclude that sol immobilization is a suitable technique for preparing gold catalysts with small particle size and narrow particle size distributions and very high activity and selectivity for benzyl alcohol oxidation.

Keywords: Solvent free oxidation; Immobilization method; Au supported catalysts; Benzyl alcohol

1. Introduction

The selective oxidation of alcohols to aldehydes or acids is an important step in the synthesis of fine chemicals. Until now, the oxidation of alcohols in industry has been mainly based on the use of stoichiometric amounts of chromate or permanganate, which are expensive and environmentally unfriendly [1–3]. Thus, today there is a strong interest in finding alternative methods that are both more economically efficient and environmentally friendly. One possible solution is the use of molecular oxygen or hydrogen peroxide in the presence of a catalyst [4,5]. The significant advantage of this method is that the main co-product is water, thus avoiding the production of highly toxic organic residues.

Heterogeneous and homogeneous catalysts have been investigated for alcohol oxidation with molecular oxygen or hydrogen peroxide in the liquid phase [6,8]. Heterogeneous catalysts seem to be more promising catalysts because of the ease of recovering and reuse. A variety of heterogeneous catalytic systems able to oxidize alcohols have been reported and the main catalytic systems are based on heteropolyacids [9,10], hydrotalcites [11–14], molecular sieves [15–17] and mixed oxides [18–21]. However, research has been historically focused on the use of Pt/C or Pd/C catalysts [22–24]. A drawback in the utilization of Pd or Pt catalysts using oxygen as the oxidant in the liquid phase is deactivation due to over-oxidation and poisoning by by-products [7]. In order to improve the lifetime of these catalysts the use of a secondary metal component, such as Bi, or Pb is advantageous in terms of activity/selectivity for various reactions and, moreover, a beneficial effect in terms of durability (lifetime) of the catalyst has been noted [8,24]. In particular, the addition of Au to Pd or Pt catalysts in the liquid phase oxidation of alcohols and polyols (sorbitol and glycerol) under mild conditions (temperature $<$ 60 °C and pressure $<$ 4 atm) improves the catalytic activity and selectivity to the desired product and also enhances the resistance to poisoning [25–27]. 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 [28]. These Au/CeO_2 catalysts were clearly demonstrated to be more active than the best supported Pd catalysts available at that time [29]. Subsequently, Corma and Domine showed [30] that this catalyst was extremely effective for the oxidation of aldehydes

---

* Corresponding author.
E-mail address: hutch@cardiff.ac.uk (G.J. Hutchings).

0920-5861/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2007.01.002

to acids. Enache et al. [31,32] have demonstrated that high activity and selectivity could be obtained using Au–Pd/TiO_2 or Au/TiO_2 catalysts when tested under solvent free conditions. In our previous studies, impregnation was the main catalyst preparation technique used and this was found to display very high catalytic activity. In this study we have extended the previous work to investigate the preparation of Au catalysts supported on carbon and titania by sol immobilization and investigated tested these materials under solvent free conditions in the liquid phase, using benzyl alcohol oxidation as the model reaction.

2. Experimental

2.1. Materials

$HAuCl_4 \cdot 3H_2O$ (99.99% purity) and activated carbon (G60) was supplied by Johnson Matthey. $NaBH_4$ of purity >96% (Aldrich) and polyvinylalcohol (PVA) (Aldrich, $M_W = 10{,}000$, 80% hydrolyzed) were used, and stock aqueous solutions of $HAuCl_4$ ([Au] = 0.05 M), PVA (1%, w/w) and $NaBH_4$ (0.1 M) were prepared.

2.2. Catalyst preparation

Monometallic catalysts based on Au and supported on titania or carbon were prepared by the immobilization of a metal sol [26].

A 1 wt% solution of PVA was added to an aqueous $HAuCl_4$ solution (1.65×10^{-4} M) with vigorous stirring (PVA/Au (w/w) = 0.65); a 0.1 M freshly prepared solution of $NaBH_4$ ($NaBH_4$/Au (mol/mol) = 5) was then added to form a metallic sol; the color of the sol was light-red (Au).

After 30 min of sol generation, the colloid was immobilized by adding activated carbon or titania (acidified at pH 1, by sulphuric acid) under vigorous stirring. The amount of support was calculated to give a total final metal loading of 1 wt%. After 2 h the slurry was filtered, the solid washed thoroughly with distilled water (2 l of doubly distilled water) to remove all the dissolved species, such as Na^+, Cl^- and dried at 120 °C overnight.

For the 1 wt% Au/TiO_2 samples three different heat treatment procedures were performed. Treatment A: the dried 1 wt% AuTiO_2 was treated at 250 °C in H_2 for 3 h, using a heating rate of 5 °C/min. Treatment B: the dried 1 wt% AuTiO_2 was treated at 250 °C in N_2 for 3 h, using a heating rate of 5 °C/min. Treatment C: the dried 1 wt% AuTiO_2 was treated at 250 °C in air for 3 h, using a heating rate of 5 °C/min.

2.3. Characterization

UV–vis spectra of sols were performed on a UV spectrometer (V-570, JASCO) in H_2O between 200 and 1200 nm, in a quartz cuvette.

X-ray photoelectron spectra were recorded on a Kratos Axis Ultra DLD spectrometer, using a monochromatised Al Kα X-ray source. Analyser pass energies of 160 eV (survey scans) or 40 eV (detailed scans) were employed, and binding energies referenced to the C 1s binding energy of adventitious carbon contamination, which was taken to be 284.7 eV.

Transmission electron microscopic investigations (TEM and HRTEM) were carried out using a Tecnai F20 transmission electron microscope operated at 200 kV (Johnson Matthey). Samples were crushed and dusted on a hollow coated copper TEM grid.

2.4. Oxidation reactions

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 (0.1 g). The autoclave was then purged five 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. 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

3.1. Characterization

UV–vis spectra (200–900 nm) of the Au sol was recorded in H_2O. For the Au sol the plasmon resonance band was located at 505 nm (Fig. 1). This band is characteristic of the plasmon resonance band of gold nanoparticles [26].

TEM micrographs of the Au sol, 1 wt% Au/TiO_2 and 1 wt% Au/C dried samples at 120 °C are shown in Fig. 2, and particle size distributions calculated from the TEM data in Fig. 3. In all cases a narrow particle size distribution was obtained as expected when using this preparation technique [27]. Mean particle sizes were 2.2 ± 0.9 nm for the Au colloid,

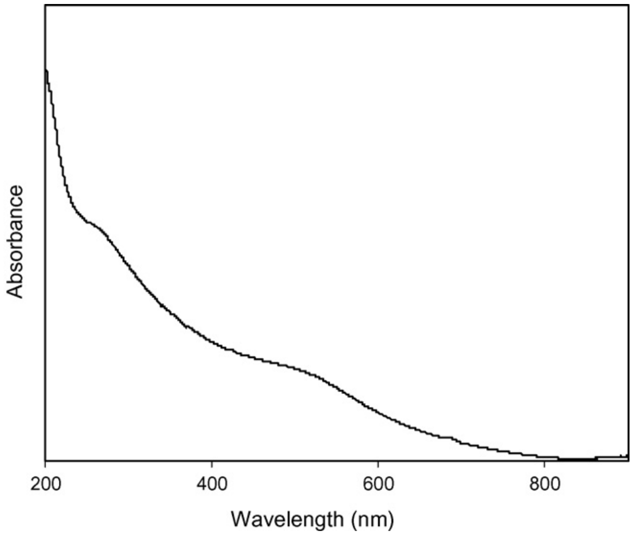


Fig. 1. UV–vis spectra of Au(0) sol.

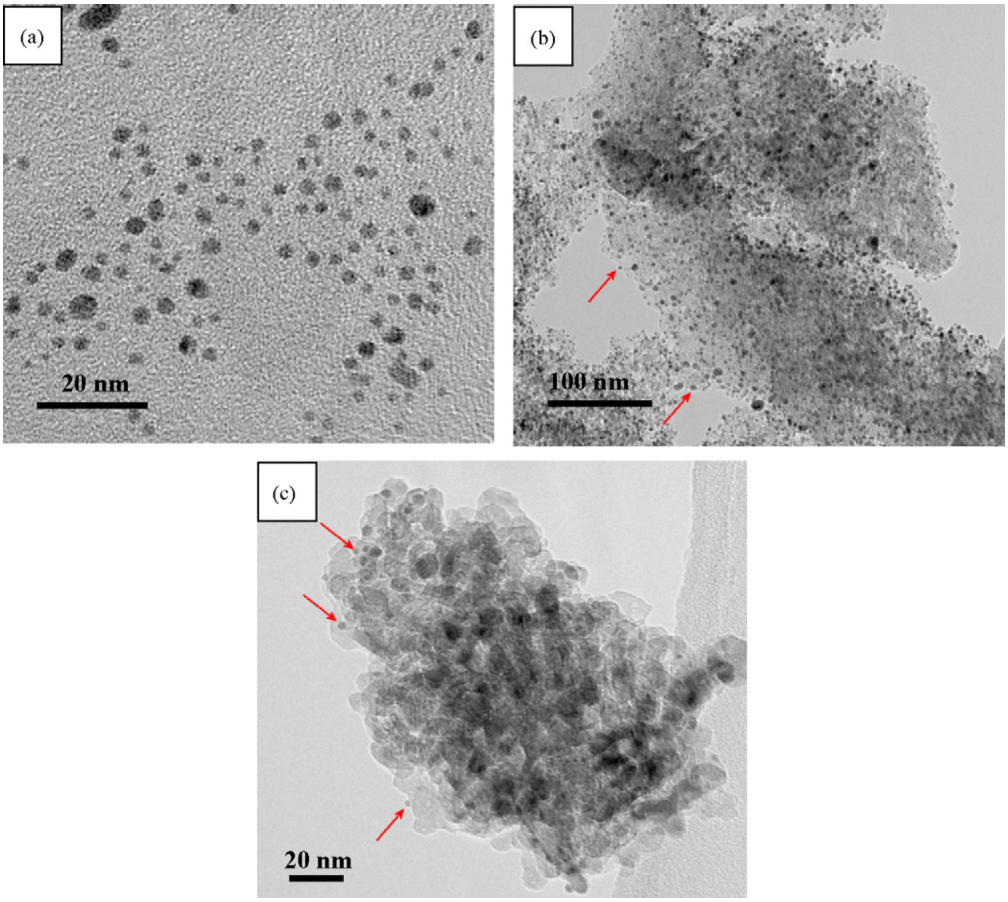


Fig. 2. TEM images of: (a) Au colloid; (b) 1% Au/C; (c) 1% Au/TiO_2.

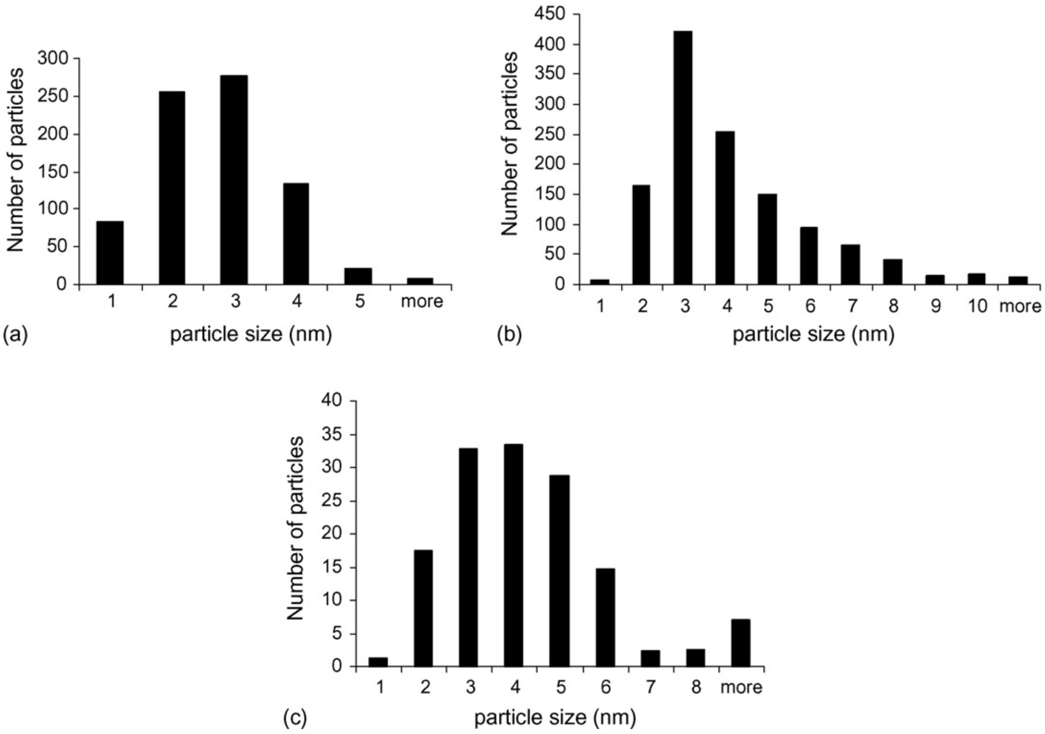


Fig. 3. Particle size distributions for: (a) Au colloid; (b) 1% Au/C; (c) 1% Au/TiO_2.

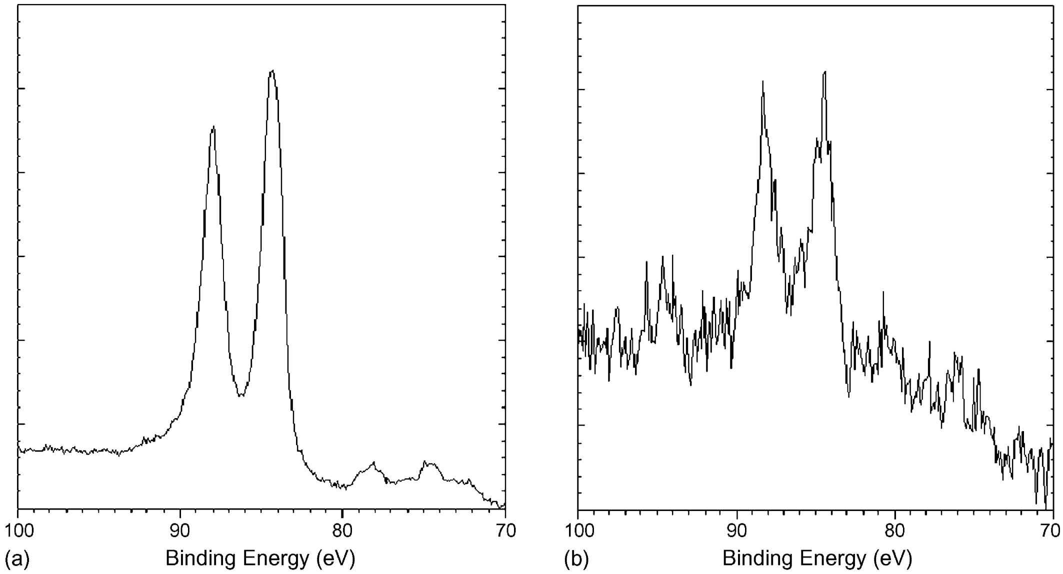


Fig. 4. XPS spectrum of the Au 4f region of: (a) 1% Au/C and (b) 1% Au/TiO_2.

3.5 ± 1.6 nm for the 1 wt% Au/C catalyst and 3.9 ± 1.9 nm for the 1 wt% Au/TiO_2 sample. Note that with both supports an increase of particle size was observed compared with the Au colloid, slightly larger particle size was observed when the colloid was immobilized on TiO_2.

XPS analysis of the Au 4f region is presented (Fig. 4). In this region the presence of gold species is indicated by the presence of two peaks (Au $4f_{7/2}$ and to the Au $4f_{5/2}$ transitions). In the following the values of binding energies (BE) will be referred to the Au $4f_{7/2}$ peak. XPS data confirmed the presence of Au in the metallic state, with an Au $4f_{7/2}$ peak observed at a binding energy of 84.2 eV (Fig. 4) for both supports, and also confirmed the absence of any contamination from sodium, chlorine and sulphur species.

The effect of the heat pre-treatment under air at 250 °C was investigated for the 1 wt% Au/C and 1 wt% Au/TiO_2 samples and it was found (Fig. 5) that a significant increase in the particle size from 3.5–3.9 to 8–10 nm occurred (mean particle were 8.7 ± 5.2 nm for the 1 wt% Au/C catalyst and 10.4 ± 4.1 nm for the 1 wt% Au/TiO_2 sample), whereas the particle size distribution are much broader. No considerable difference between TiO_2 and C samples has been revealed. XPS measurements of the carbon region indicated the presence of a higher carbon content for the dried 1 wt% Au/TiO_2, whereas for the treated 1 wt% Au/TiO_2 samples a considerable loss of carbon was observed, indicating that the adsorbed layer around gold particle and on the TiO_2 surface has been significantly diminished during heat treatment in agreement with previous results [33].

3.2. Benzyl alcohol oxidation

The oxidation of benzyl alcohol is often used as a model reaction for alcohol oxidation, not only due to its relatively high reactivity but also because of the existence of a complex reaction network (Scheme 1). The target products are benzaldehyde and benzoic acid, but other by-products, *e.g.* toluene, benzene, benzyl benzoate and acetal can form

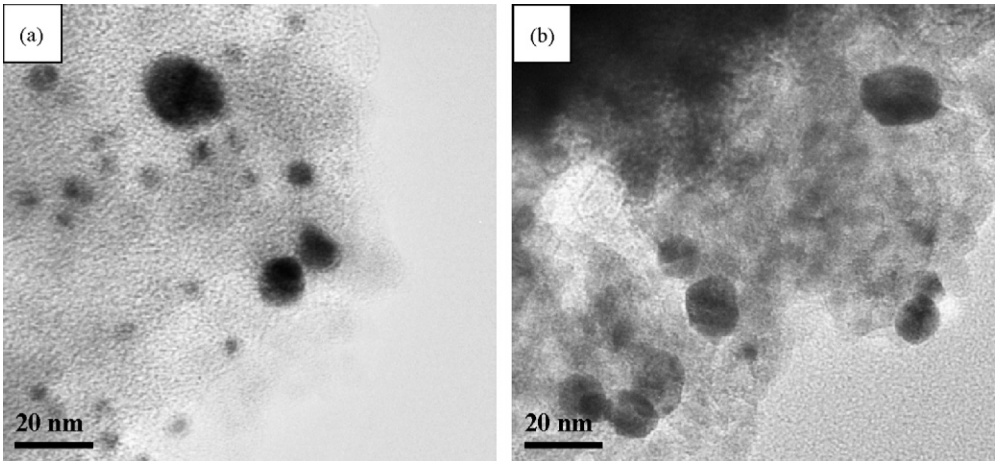
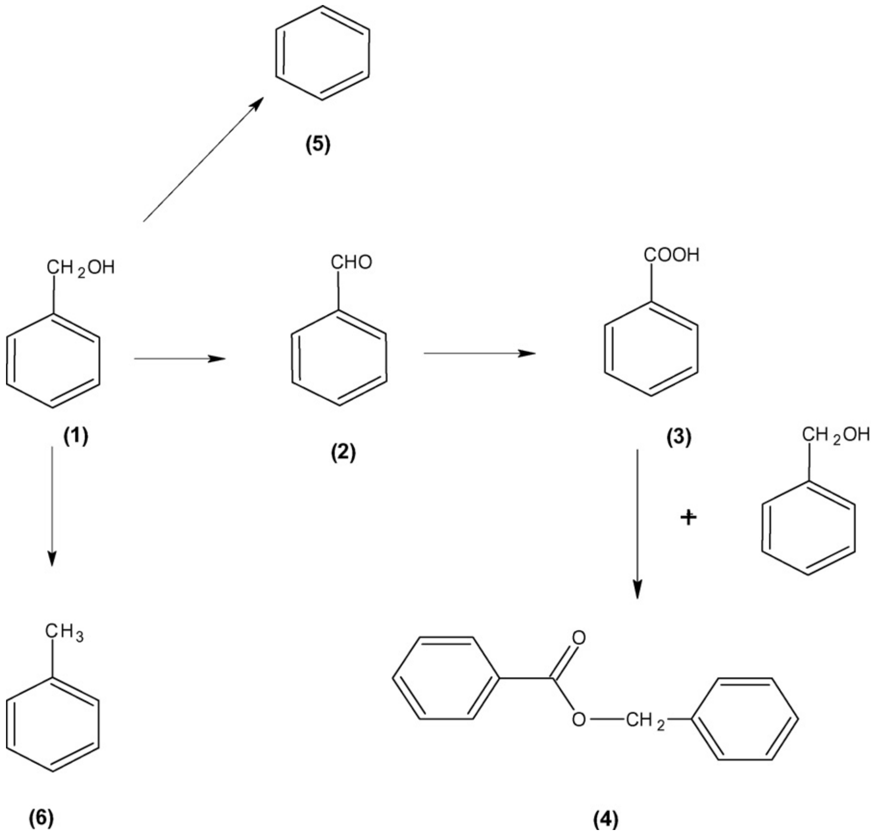


Fig. 5. TEM images of: (a) 1% Au/C and (b) 1% Au/TiO_2 after calcinations at 250 °C under air for 3 h.



Scheme 1. General reaction pathway for benzyl alcohol: (1) benzyl alcohol; (2) benzaldehyde; (3) benzoic acid; (4) benzyl benzoate; (5) benzene; (6) toluene.

depending on the reaction conditions and metal catalyst employed [14,31,32]. These by-products are likely to be the outcome of side reactions due to hydrogenolysis (toluene formation), decarbonylation (benzene) and esterification reaction pathways (benzyl benzoate) (see Scheme 1) [14,32].

3.2.1. Activity of monometallic catalysts prepared by the immobilization method

The catalytic data are shown in Tables 1 and 2. The reaction profiles of 1 wt% Au/TiO$_2$ and of 1 wt% Au/C as a function of time are shown in Figs. 6 and 7, respectively. In the case of 1 wt% Au/TiO$_2$, increase of conversion was accompanied with a decrease in the selectivity to benzaldehyde. The main by-products observed were benzoic acid and benzyl benzoate. These results showed that benzoic acid was the over-oxidation product of benzaldehyde, whereas the formation of benzyl benzoate was due to the esterification reaction of the benzoic acid and benzyl alcohol in agreement with previous reported results [14,32]. In the case of 1 wt% Au/C, a similar reaction profile was found. However, the decrease in selectivity to benzaldehyde as the reaction was proceeding was higher with respect to 1 wt% Au/TiO$_2$ catalyst. The major by-products were benzoic acid followed by toluene formation.

In terms of activity 1 wt% Au/C was more active than 1 wt% Au/TiO$_2$ by a factor of 1.5 based on the TOF as it is shown in Table 1. With 1 wt% Au/TiO$_2$ a higher yield to benzaldehyde (40.5%) was obtained than 1 wt% Au/C (30.8%).

For evaluating which catalyst is the most selective toward the desired product, comparison at *iso*-conversion was chosen (*e.g.* at 50% conversion) as products selectivity were observed to vary markedly with conversion. In Table 2 the summary of the product distribution selectivity's are presented. At 50%

Table 1
Liquid phase oxidation of benzyl alcohol for catalysts containing 1 wt% of metal prepared by the sol immobilization method[a]

Catalysts	Conversion (%)	Selectivity (%)			Yield (%)			TOF (h^{-1})[b]
		Toluene	Benzaldehyde	Benzoic acid	Toluene	Benzaldehyde	Benzoic acid	
Au/TiO$_2$	55	5.6	73.7	15.1	3.1	40.5	8.3	9,780
Au/TiO$_2$ (treated/250 °C/H$_2$)	67	11.3	63.7	20.5	7.6	42.7	13.8	14,900
Au/TiO$_2$ (treated/250 °C/N$_2$)	66	11.8	61.6	21.6	7.8	40.8	14.3	10,500
Au/TiO$_2$ (treated/250 °C/air)	68	19.7	54.7	20.5	13.5	37.4	14.0	31,900
Au/C	48	5.8	64.4	22.8	2.8	30.8	10.9	14,800

[a] Reaction conditions: benzyl alcohol, 0.1 g of catalyst, $T = 160$ °C, $pO_2 = 10$ bar, time of reaction = 6 h, stirring rate 1500 rpm.
[b] TOF (h^{-1}) at 0.5 h of reaction. TOF numbers were calculated on the basis of total loading of metals.

Table 2
Liquid phase oxidation of benzyl alcohol for catalysts containing 1 wt% of metal prepared by the sol immobilization method[a]

Catalysts	Selectivity at 50% conversion S_{50} (%)						TOF (h^{-1})[b]
	Benzene	Toluene	Benzaldehyde	Benzoic acid	Benzyl benzoate	Acetal	
Au/TiO_2	0.5	6.7	77.0	11.0	4.7	0.1	9,780
Au/TiO_2 (treated/250 °C/H_2)	0.5	17.1	70.2	8.7	3.4	0.1	14,900
Au/TiO_2 (treated/250 °C/N_2)	0.6	14.1	68.7	12.9	3.6	0.1	10,500
Au/TiO_2 (treated/250 °C/air)	0.5	21.7	64.2	9.9	3.7	0	31,900
Au/C	0.7	5.2	63.5	24.2	6.5	0.0	14,800

Product distribution selectivities determined at *iso*-conversion (50%).

[a] Reaction conditions: benzyl alcohol, 0.1 g of catalyst, $T = 160$ °C, $pO_2 = 10$ bar, time of reaction = 6 h, stirring rate 1500 rpm.

[b] TOF (h^{-1}) at 0.5 h of reaction. TOF numbers were calculated on the basis of total loading of metals. S_{50} indicate the selectivity observed at 50% conversion.

conversion the most selective catalyst toward benzaldehyde formation was 1 wt% Au/TiO_2 (77%), whereas 1 wt% Au/C exhibited a much lower selectivity to benzaldehyde (63.5%). Interestingly, the two-fold increase in the selectivity to benzoic acid with 1 wt% Au/C with respect to 1 wt% Au/TiO_2 (24.2% for 1 wt% Au/C and 11.0% for 1 wt% Au/TiO_2) indicates that over-oxidation of benzaldehyde to benzoic acid occurs to a higher extent with the 1 wt% Au/C catalyst.

These results indicate the importance of the choice of support for the gold nanoparticles. Since a similar particle size exists for both support materials, the difference observed in catalytic activity and selectivity may be attributed to other factors, such as the metal support interaction and the shape of the particles as it has been suggested previously [33,34]. In fact, as it is shown in Fig. 3 the gold colloids in the solution appear to have a spherical shape. However, when the gold colloids were adsorbed on the support material (carbon or titania) it seems that the shape of the gold particles was influenced from the support interaction. It has been claimed that different geometries of the gold particles are possible on each of the support, which could lead to different faceting and creation of defect sites and thus affecting the catalytic properties of the supported Au particles [33,34]. Nevertheless, further investigations are needed for a better understanding of the parameters affecting the catalytic activity of the aforementioned gold catalysts.

3.2.2. Effect of heat treatment procedure

We have previously demonstrated the importance of the heat treatment procedure on the morphology of the catalyst and thus on the catalytic activity [35]. However, the catalysts discussed in this work have been prepared differently, using sol immobilization with PVA as protecting agent, and $NaBH_4$ to reduce the gold precursor. With these newly prepared catalysts we expect that heat treatment will result in the removal of a significant amount of the protecting agent (PVA) from the surface of the metal, thus leading to a significant increase in the accessibility of the gold surface area and in addition, the metal particle size distribution might also be affected by the heat treatment.

The 1 wt% Au/TiO_2 catalysts were subjected to three different treatments at 250 °C, being treated in H_2, N_2 and air flow. The results of the different treatment procedures are presented in Table 1, and the reaction profiles of the treated catalysts as a function of time are shown in Fig. 8. With increase of conversion the selectivity to benzaldehyde followed a decline, whereas selectivity toward benzoic acid

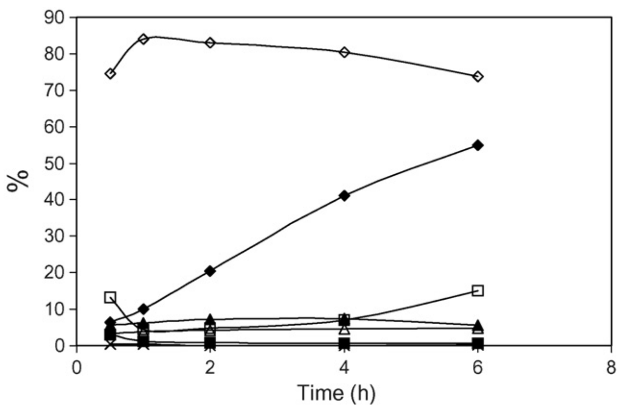


Fig. 6. Selective oxidation of benzyl alcohol in the presence of 1 wt% Au/TiO_2(I). Reaction conditions: benzyl alcohol 40 ml, 0.1 g of catalyst, $T = 160$ °C, $pO_2 = 10$ bar, time of reaction = 6 h, stirring rate 1500 rpm. (◆) Benzyl alcohol conversion (%), (■) benzene selectivity (%), (▲) toluene selectivity (%), (◇) benzaldehyde selectivity (%), (□) benzoic acid selectivity (%), (△) benzyl benzoate selectivity (%) and (×) acetal selectivity (%).

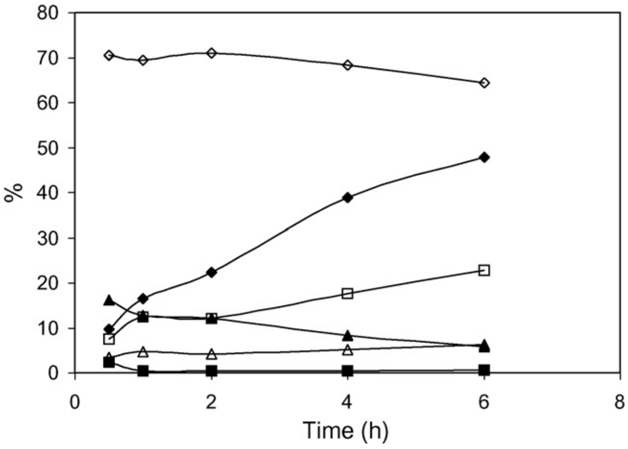


Fig. 7. Selective oxidation of benzyl alcohol in the presence of 1 wt% Au/C(I). Reaction conditions: benzyl alcohol 40 ml, 0.1 g of catalyst, $T = 160$ °C, $pO_2 = 10$ bar, time of reaction = 6 h, stirring rate 1500 rpm. (◆) benzyl alcohol conversion (%), (■) benzene selectivity (%), (▲) toluene selectivity (%), (◇) benzaldehyde selectivity (%), (□) benzoic acid selectivity (%), (△) benzyl benzoate selectivity (%) and (×) acetal selectivity (%).

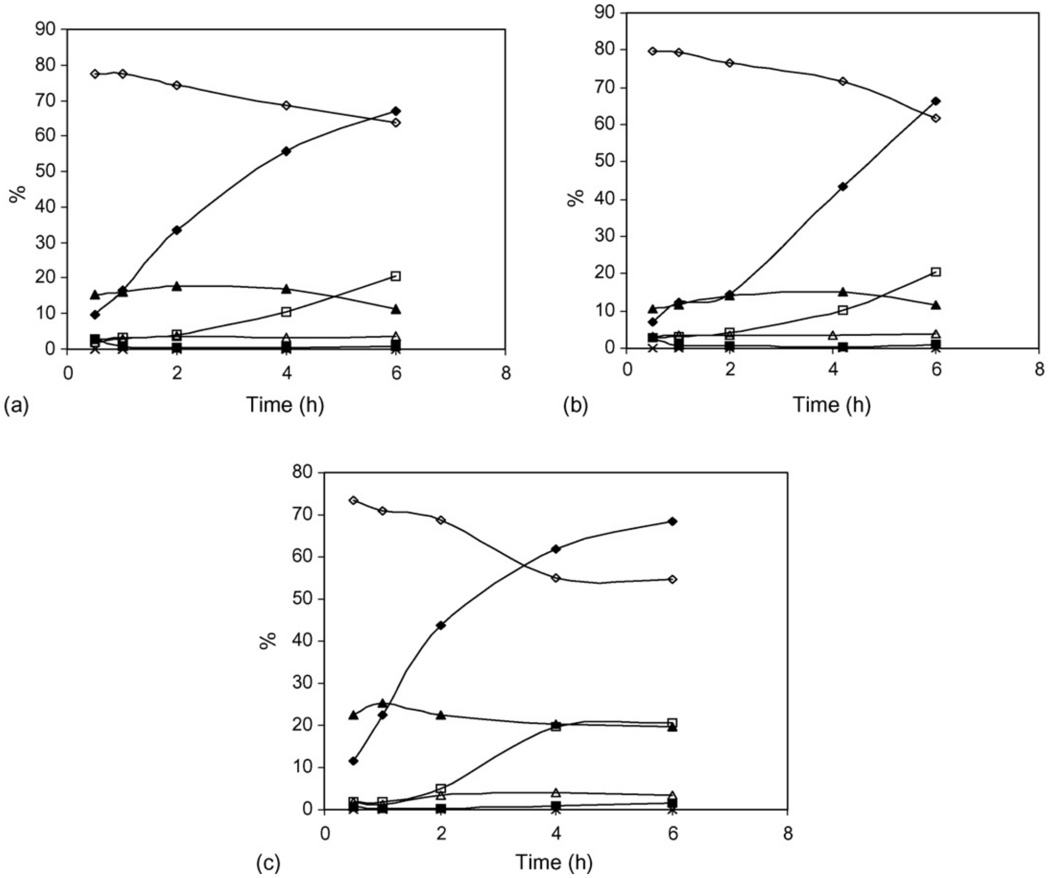


Fig. 8. Selective oxidation of benzyl alcohol in the presence of 1 wt% Au/TiO$_2$(I): (a) 1 wt% Au/TiO$_2$ treated under H$_2$ at 250 °C for 3 h; (b) 1 wt% Au/TiO$_2$ treated under N$_2$ at 250 °C for 3 h; (c) 1 wt% Au/TiO$_2$ treated under air at 250 °C for 3 h. Reaction conditions: benzyl alcohol 40 ml, 0.1 g of catalyst, $T = 160$ °C, $pO_2 = 10$ bar, time of reaction = 6 h, stirring rate 1500 rpm. (◆) Benzyl alcohol conversion (%), (■) benzene selectivity (%), (▲) toluene selectivity (%), (◇) benzaldehyde selectivity (%), (□) benzoic acid selectivity (%), (△) benzyl benzoate selectivity (%) and (×) acetal selectivity (%).

increased, indicating the consecutive oxidation of benzaldehyde to benzoic acid. Moreover, toluene formation was observed from the beginning of the reaction and at low conversion (<10%), suggesting that it is a primary product. Following the progress of the reaction, selectivity to toluene reached a maximum value and then decreased with further increases in conversion. In addition, benzyl benzoate formation was observed, which was slightly increasing as the reaction was proceeding. It is evident in Table 2 that heat treatment was beneficial in terms of activity in all cases and that there is a significant influence of the nature of the gas stream used in the heat treatment on the distribution of the products when the materials are used as catalysts for the oxidation of benzyl alcohol. The highest activity was obtained (indicated by TOF) when air was used, followed by H$_2$ and finally N$_2$. The increase of activity due to heat treatment can probably be ascribed to the removal of the protecting agent from the surface of the TiO$_2$ and the metal as indicated by XPS (reduction of carbon content). However, we cannot exclude the possible role of particle size, since a significant growth from 3.5–3.9 to 8–10 nm was observed during heat treatment under air. In terms of distribution of products, a decrease in the selectivity to benzaldehyde was observed coupled with an increase in toluene formation. These results suggest that the heat treatment procedure possibly increases the number of gold sites responsible for toluene formation; which could be due to the removal, by heat treatment, of residual polymer, which is blocking the these gold sites. Furthermore, the formation of toluene is due to hydrogenolysis of the C–O bond in benzyl alcohol and may also indicates the presence of surface hydrogen on the Au surface. If the accessible gold surface area has increased after heat treatment, it is possible that a higher amount of Au–H species will exist during reaction, thus facilitating toluene formation. Recently Abad et al. showed the existence of Au–H species in the aerobic oxidation of alcohols [28]. Moreover, they correlated the selectivity of aerobic oxidation of alcohols with respect to the stability and concentration of Au–H species [36]. Nevertheless, we cannot exclude the modification of particle size and especially shape when the treatment under N$_2$ or H$_2$ was performed and the development of specific planes of Au particles that favor toluene formation. It has been shown that the treatment under different gases modifies to a specific extent the particle size and shape of the gold particles [37]. Nevertheless, detailed structural studies by HREM are required for giving answers about the shape of gold particles during heat treatment and correlating with the catalytic properties.

4. Conclusions

We have explored, for the first time, the catalytic activity of gold monometallic catalysts prepared by sol immobilization in the selective oxidation of benzyl alcohol under solvent free conditions. The sol immobilization preparation produced gold catalysts with narrow metal particle size distributions of *ca.* 3 nm mean particle size that displayed very high activity (TOF $\sim$ 31,900 h^{-1}), superior to those previously reported that were prepared by impregnation methods. The choice of support affected product distributions and the activity of gold catalysts, providing clear evidence that the chemical nature of the support is also important. Generally, when TiO_2 was used as support, substantial differences in terms of activity and distribution of products were observed between the two supports. Furthermore, the choice of heat treatment influences significantly the activity and the distribution of products.

Acknowledgments

The authors are grateful for financial support from the EPSRC and the Auricat EU network (HPRN-CT-2002-00174) and Dr. Peter Bishop, Dr. Benedicte Thiebaut, Dr. James Cookson and Dr. Gregg Goodlet from Johnson Matthey for the TEM analysis.

References

[1] G. Cainelli, G. Cardillo, Chromium Oxidations in Organic Chemistry, Springer-Verlag, Berlin, 1984.
[2] F.A. Luzzio, Organic Reactions, vol. 53, Wiley, New York, 1998, p. 1.
[3] T.T. Tidwell, Organic Reactions, vol. 39, Wiley, New York, 1990, p. 297.
[4] R.A. Sheldon, I.W.C.E. Arends, A. Dijksman, Catal. Today 57 (2000) 157.
[5] R.A. Sheldon, I.W.C.E. Arends, G.J. Brink, A. Dijksman, Acc. Chem. Res. 35 (2002) 774.
[6] M. Besson, P. Gallezot, Catal. Today 57 (2000) 127.
[7] T. Mallat, A. Baiker, Catal. Today 19 (1994) 247.
[8] T. Mallat, A. Baiker, Chem. Rev. 104 (2004) 3037.
[9] R. Neumann, M. Levin, J. Org. Chem. 56 (1991) 5707.
[10] S. Fujibayashi, K. Nakayama, M. Hamamoto, S. Sakaguchi, Y. Nishiyama, Y. Ishii, J. Mol. Catal. 110 (1996) 105.
[11] K. Kaneda, K. Yamaguchi, K. Mori, T. Mizugaki, K. Ebitani, Catal. Surv. Jpn. 4 (2000) 31.
[12] K. Kaneda, T. Yamashita, T. Matsushita, K. Ebitani, J. Org. Chem. 63 (1998) 1750.
[13] B.M. Choudary, M.L. Kantam, A. Rahman, C.V. Reddy, K.K. Rao, Angew. Chem. Int. Ed. 40 (2001) 763.
[14] V.R. Choudhary, P.A. Chaudhari, V.S. Narkhede, Catal. Commun. 4 (2003) 171.
[15] M.G. Clerici, Top. Catal. 13 (2000) 373.
[16] J.D. Chen, J. Dakka, E. Neeleman, R.A. Sheldon, J. Chem. Soc. Chem. Commun. (1993) 1379.
[17] J.D. Chen, H.E.B. Lempers, R.A. Sheldon, Colloid Surf. A 101 (1995) 137.
[18] M. Musawir, P.N. Davey, G. Kelly, I.V. Kozhevnikov, Chem. Commun. (2003) 1414.
[19] H.B. Ji, T. Mizugaki, K. Ebitani, K. Kaneda, Tetrahedron Lett. 43 (2002) 7179.
[20] H.B. Ji, K. Ebitani, T. Mizugaki, K. Kaneda, Catal. Commun. 3 (2002) 511.
[21] H.B. Ji, K. Ebitani, T. Mizugaki, K. Kaneda, React. Kinet. Catal. Lett. 78 (2003) 73.
[22] A.B. Crozon, M. Besson, P. Gallezot, New J. Chem. 22 (1998) 269.
[23] P. Vinke, D. deWit, A.T.J.W. de Goede, H. van Bekkum, New Developments in Selective Oxidation by Heterogeneous Catalysis, Studies in Surface Science and Catalysis, vol. 72, Elsevier, Amsterdam, 1992, p. 1.
[24] P. Gallezot, Catal. Today 37 (1997) 405.
[25] N. Dimitratos, F. Porta, L. Prati, A. Villa, Catal. Lett. 99 (2005) 181.
[26] C.L. Bianchi, P. Canton, N. Dimitratos, F. Porta, L. Prati, Catal. Today 102 (2005) 203.
[27] N. Dimitratos, J.A. Lopez-Sanchez, D. Lennon, F. Porta, L. Prati, A. Villa, Catal. Lett. 108 (2006) 147.
[28] A. Abad, P. Concepción, A. Corma, H. García, Angew. Chem. Int. Ed. 44 (2005) 4066.
[29] K. Mori, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, J. Am. Chem. Soc. 26 (2004) 10657.
[30] A. Corma, M.E. Domine, Chem. Commun. (2005) 4042.
[31] D.I. Enache, J.K. Edwards, P. Landon, B. Solsona-Espriu, A.F. Carley, A.A. Herzing, M. Watanabe, C.J. Kiely, J.D.W. Knight, G.J. Hutchings, Science 311 (2006) 362.
[32] D.I. Enache, D.W. Knight, G.J. Hutchings, Catal. Lett. 103 (2005) 43.
[33] M. Comotti, W.C. Li, B. Spliethoff, F. Schüth, J. Am. Chem. Soc. 128 (2006) 917.
[34] M.S. Chen, D.W. Goodman, Catal. Today 111 (2006) 22.
[35] J.K. Edwards, B.E. Solsona, P. Landon, A.F. Carley, A. Herzing, C.J. Kiely, G.J. Hutchings, J. Catal. 236 (2005) 69.
[36] A. Abad, C. Almela, A. Corma, H. Garcia, Chem. Commun. (2006) 3178.
[37] R. Zanella, C. Louis, Catal. Today 107/108 (2005) 768.