



Selective suppression of disproportionation reaction in solvent-less benzyl alcohol oxidation catalysed by supported Au–Pd nanoparticles

Enhong Cao^{a,b}, Meenakshisundaram Sankar^c, Ewa Nowicka^c, Qian He^d, Moataz Morad^c, Peter J. Miedziak^c, Stuart H. Taylor^c, David W. Knight^c, Donald Bethell^e, Christopher J. Kiely^d, Asterios Gavriilidis^{a,b,*}, Graham J. Hutchings^{c,**}

^a Department of Chemical Engineering, University College London, Torrington Place, London WC1E 7JE, UK

^b Materials Chemistry Centre, University College London, 20 Gordon Street, London WC1H 0AJ, UK

^c Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, UK

^d Department of Materials Science and Engineering, Lehigh University, 5 East Packer Avenue, Bethlehem, PA 18015-3195, USA

^e Department of Chemistry, University of Liverpool, Liverpool L69 3BX, UK

ARTICLE INFO

Article history:

Received 2 November 2011

Received in revised form 2 May 2012

Accepted 14 May 2012

Available online 17 July 2012

Keywords:

Gold palladium catalysts

Alcohol oxidation

Benzyl alcohol oxidation

ABSTRACT

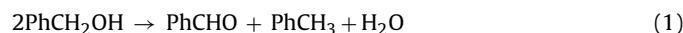
Disproportionation of benzyl alcohol has been identified as the source of toluene formation in the solvent free oxidation of benzyl alcohol using supported gold palladium catalysts. There is a slight increase in the disproportionation reaction, and hence the toluene selectivity, when this reaction is performed in a continuous mode using a micro-packed bed reactor when compared to the same reaction performed in a conventional glass stirred batch reactor. Oxidation and disproportionation reactions respond slightly differently to the changes in reaction parameters, like oxygen concentration and pressure, when a micro packed bed reactor was used instead of a conventional glass stirred reactor. When MgO supported gold–palladium catalysts were used for this reaction, the toluene selectivity reduced substantially at the cost of conversion.

© 2012 Elsevier B.V. Open access under [CC BY](http://creativecommons.org/licenses/by/3.0/) license.

1. Introduction

Selective oxidation of alcohols, using molecular oxygen, has received considerable attention in the recent past due to its potential application in the production of intermediates in the fine chemicals and fragrance industries [1–3]. Many heterogeneous catalysts have been reported to be active for this transformation and recently supported gold nanoparticles have been shown to be highly effective [4–6]. With respect to gold catalysis, it is known that this reactivity is due to small gold nanoparticles; their interface with the supporting matrix is also important [7–10]. Recently, we reported a twenty five fold increase in turnover frequency for the oxidation of alcohols by adding small amounts of palladium to supported gold catalysts and we showed that they can be used for the solvent-free aerobic oxidation of alcohols [11]. Subsequently bimetallic gold–palladium catalysts have been utilized for the oxidation of a wide range of substrates including aliphatic alcohols,

polyols and alkyl aromatics [12–14]. Benzyl alcohol has long been used as a model substrate for selective oxidation [15–17]. Earlier investigations on the solvent-free aerobic oxidation of this substrate using supported gold–palladium catalysts resulted in the detection of many products, including toluene, benzoic acid, benzyl benzoate and dibenzyl ether, besides the desired product benzaldehyde [15–18]. A detailed knowledge of the origins of these products is crucial to fine-tune the catalyst to obtain the most important product, benzaldehyde, in high yield by suppressing the formation of by-products. Benzaldehyde and benzoic acid are formed by the sequential oxidative dehydrogenation and further oxidation of benzyl alcohol. Dibenzyl ether is formed by the dehydration of benzyl alcohol, and benzyl benzoate is reported to be formed either via hemi-acetal from benzaldehyde or by the esterification of benzoic acid by the substrate; benzyl alcohol [12,18,19]. There has been a long debate on the origin of the other major by-product: toluene [12,20–22]. Baiker *et al.*, proposed hydrogenolysis of benzyl alcohol as the origin of toluene but many other groups proposed a disproportionation mechanism of benzyl alcohol as the origin of toluene [12,20–22]. Disproportionation of benzyl alcohol results in an equimolar mixture of benzaldehyde and toluene as shown in reaction (1).



* Corresponding author at: Department of Chemical Engineering, University College London, Torrington Place, London WC1E 7JE, UK.

** Corresponding author. Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, 8 UK.

E-mail addresses: a.gavriilidis@ucl.ac.uk (A. Gavriilidis), Hutch@cf.ac.uk (G.J. Hutchings).

Since benzaldehyde is formed by both oxidation as well as disproportionation reactions, it becomes difficult to study this disproportionation reaction under aerobic conditions, where both oxidation as well as disproportionation reactions are active [23]. Recently we reported a methodology to quantify these two reactions separately, even under such aerobic conditions [23]. Based on this methodology, we found that the oxidation and disproportionation reaction could have different active sites in the supported gold palladium catalysts; metal sites for the oxidation reaction and metal–support interface sites for the disproportionation reaction. We have also demonstrated that by changing the support, we can either switch-on or switch-off this disproportionation reaction and thus toluene formation [12,23]. All the above mentioned results were obtained in a conventional glass stirred reactor (GSR) operated in a batch mode. Industrially, reactions operated in a continuous mode are more attractive and many catalytic reactions display a change in product selectivity when operated in continuous-flow conditions when compared to batch mode operation.

For gas–liquid–solid multiphase reactions, packed-bed flow reactor systems have the advantages of simplifying the process by eliminating separation of liquid products and solid catalyst. Performing these reactions continuously over a longer time period permits insight into the stability of the catalyst, by comparison of its performance using conventional batch reactor or autoclave. For most multiphase reactions, where mass transfer can be a limiting factor, micro-reactors offer improved overall reaction rates and reactor performance when compared with conventional macro-reactors [24–26]. The small channel of the micro-reactor enables efficient gas–liquid mixing and sufficient gas–liquid–solid contact, leading to improved mass transfer in the packed catalyst bed. For highly exothermic reactions, uniform temperature control throughout the reactor can be easily achieved by virtue of the high surface-to-volume ratio [27]. The small internal reactor volume also lowers the consumption of raw materials, thereby improving both safety and economy.

In an attempt to understand the effect of using such micro-reactors on the two reactions of interest; the oxidation and disproportionation reactions of benzyl alcohol using supported gold–palladium nanoalloys, we have compared the outcomes from these reactions under various reaction conditions in two different reactors; namely, conventional glass stirred batch reactor (GSR) and a micro packed bed reactor (MPBR) and report the results obtained herein.

2. Experimental

2.1. Catalyst preparation

For the preparation of 1%(Au–Pd)/TiO₂ and 1%Au–Pd/MgO catalysts, aqueous solutions of PdCl₂ (Sigma Aldrich) and HAuCl₄·3H₂O (Sigma Aldrich) of the desired concentrations were prepared. Polyvinyl alcohol (PVA) (1 wt% aqueous solution, Aldrich, MW = 10,000, 80% hydrolysed) and an aqueous solution of NaBH₄ (0.1 M) were also prepared. To a mixed aqueous PdCl₂ and HAuCl₄ 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 NaBH₄ (0.1 M, NaBH₄/(Au + Pd) (mol/mol) = 5) was then added to form a dark-brown sol. After 30 min of sol generation, the colloid was immobilized by adding the solid support [TiO₂ (Degussa, P25), MgO (BDH)] and acidified to pH 1 by concentrated sulphuric acid under vigorous stirring in the case of TiO₂, acid was not added when MgO was used as the support. The amount of support material required was calculated so as to have a total final metal loading of 1 wt% with a metal ratio of 1:1 molar. After 2 h, the

slurry was filtered, the catalyst washed thoroughly with distilled water (neutral mother liquors) and dried at 120 °C overnight under static air. The filtrate solution was checked for the presence of Au and Pd. It was found that there were no metal ions in the filtrate, indicating that all the metals are immobilized on to the support.

2.2. Catalyst characterisation using scanning transmission electron microscopy

The 1%(Au–Pd)/TiO₂ and 1%Au–Pd/MgO catalysts have been extensively studied previously [23,28,29,18] and it has been found that particle size and composition are important factors and for that reason we extend these studies by scanning transmission electron microscopy (STEM). Samples for examination by TEM were prepared by dry dispersing the catalyst powder onto a holey carbon film supported by a 300 mesh copper TEM grid. STEM high angle annular dark field (HAADF) images and X-ray energy-dispersive spectra (XEDS) of individual nanoparticles were obtained using an aberration corrected JEOL 2200FS STEM operating at 200 kV and equipped with a Thermo Scientific Inc. Si(Li) detector for XEDS.

2.3. Catalytic performance in a glass stirred reactor (GSR)

Benzyl alcohol oxidation was carried out in a Radleys carousel reactor using a 50 mL glass stirred reactor. In a typical reaction, the requisite amount of catalyst and substrate were charged into the reactor at room temperature which was then purged with the required gas (O₂, He or air) three times before the reactor was sealed using a Teflon screw threaded cap. The reactor was always connected to the gas line to ensure that any gas consumed was replenished. The pressure was measured using a gauge fitted to the inlet line. There was no change in the pressure during the course of the reaction. The reactor with the reaction mixture was loaded into a preheated heating block, which was maintained at the reaction temperature. The reaction was started by switching on the stirring inside the reactor with a magnetic bar at 1000 rpm. After a specific time, the stirring was stopped and the reactor was immediately cooled in an ice bath. After cooling for 10 min, the reactor was opened carefully and the contents were centrifuged. An aliquot of the clear supernatant reaction mixture (0.5 mL) was diluted with mesitylene (0.5 mL) for GC analysis. It was established that no reaction occurred in the absence of the Au–Pd catalyst or in the presence of the catalyst support alone. Mass transfer was found not to be rate-limiting at a stirring speed of 500 rpm or above. The turnover numbers for individual reactions; oxidation (TON_O), disproportionation (TON_D) and the total turnover number TON_{Tot} were calculated using the following equations [23]:

$$\text{TON}_D = \frac{2 * \text{mol}_{\text{tol}}}{\text{mol}_{\text{metal}}}$$

$$\text{TON}_O = \frac{\text{mol}_{\text{PhCHO}} - \text{mol}_{\text{tol}}}{\text{mol}_{\text{metal}}}$$

$$\text{TON}_{\text{Tot}} = \frac{\text{mol}_{\text{PhCH}_2\text{OH converted}}}{\text{mol}_{\text{metal}}}$$

2.4. Catalytic performance in a micro-packed bed reactor (MPBR)

The micro-packed bed reactor chips were made of silicon and glass with an overall size of 23 mm × 23 mm [18]. The dimension of the reaction channel was 0.6 mm (W) × 0.3 mm (H) × 190 mm (L). The prepared catalyst powder was pelletized and the desired particle size (53–63 μm) fraction was obtained by crushing and sieving. The catalyst was then introduced into the reaction channel through

the gas inlet with the help of vacuum at the outlet of the reaction channel. The prepared reactor was assembled with a heating block and insulation for flow connection and temperature control. Liquid alcohol (benzyl alcohol, 99.98%, Sigma–Aldrich) was delivered into the reactor by a syringe pump (PhD Ultra, Harvard Apparatus). Gases were regulated by mass flow controllers (Brooks 5850TR) and directed to the gas inlet of the reactor. The effluent from the reactor was passed into a small glass vial (2 mL) which was located in a cold trap (ice-water bath), where gas and liquid were separated and the liquid product collected. Quantitative analysis was carried out using an Agilent 6890 GC with FID, and a HP-INNOWax (19091-133) capillary column and an auto-liquid-sampler. For GC analysis, 10 μ L of the collected sample was diluted using 0.5 mL of mesitylene containing decane as an internal standard. Experiments were started by setting the reactor temperature, gas flow rate and the alcohol flow rate to desired values. All the gas flow rates reported are in mL/min at Standard Temperature and Pressure (STP, 0 °C and 1.01325 bar). Once the reactor reached the set temperature, the reaction was carried out for another 20 min to stabilize the reaction system. Collection of reaction products was then started using a new sample vial. The first sample was taken and analysed after 40 min and the second sample after another 20 min. Benzyl alcohol conversion (X) was calculated from the measured concentration of the alcohol in the outlet of the reactor:

$$X = \frac{C_{\text{alcohol, in}} - C_{\text{alcohol, out}}}{C_{\text{alcohol, in}}} \times 100\%$$

Selectivity to product (S_i) was calculated as the moles of the alcohol converted into the product divided by the total mole of the alcohol converted:

$$S_i = \frac{C_{i, \text{out}} \gamma_i}{C_{\text{alcohol, in}} X} \times 100\% \quad i \neq \text{alcohol}$$

where γ_i is the mole number of the alcohol needed to produce 1 mol of the product. The carbon balance was within $\pm 5\%$. The silicon–glass micro-reactor was inert to the reaction which was verified by running a blank test with inert glass beads packed into the reactor channel at 140 °C. During the experimental parameter study, the reactor was kept at 40 °C overnight with flowing oxygen. Reproducibility of the experiments and the stability of the catalyst were checked by restarting the experiment with a standard run (100 °C, O₂ 0.3 mL/min, alcohol 0.003 mL/min) or repeating one set of conditions run on the previous day. The relative differences between the standard run were found to be less than $\pm 3\%$.

3. Results and discussion

3.1. Effect of temperature on disproportionation of benzyl alcohol

Solvent-free benzyl alcohol reaction, under anaerobic conditions, was performed using a 1%Au–Pd/TiO₂ catalyst, prepared by a sol-immobilization technique, in a MPBR at different temperatures. TON_{Tot}, TON_O, TON_D were calculated, using the procedure described in Section 2, and are given in Fig. 1A. In the case of the GSR the TON_{Tot} was not equivalent to TON_D under anaerobic conditions, as there was a small positive value for TON_O was attributed to the adsorbed O₂ on the surface of the catalyst, which could not be removed [23]. When the same reaction was performed in a MPBR under anaerobic conditions, TON_O was always very close to zero (Fig. 1A) because of the complete removal of adsorbed O₂ in the MPBR. The product mixture comprised of near equivalent amounts of benzaldehyde and toluene ($\pm 2\%$) (Fig. 1B). This further proves that, under anaerobic conditions, disproportionation is the only active reaction and indicates that this could be the source of

Table 1
Comparison of TON_D at anaerobic and aerobic conditions in MPBR.^a

T (°C)	Anaerobic condition		Aerobic condition	
	TON _D	TON _O	TON _D	TON _O
80	545		1889	4546
100	1113		4378	5611
120	1933		8446	3442
140	3741		10,770	1799

^a Reaction conditions: benzyl alcohol: 0.003 mL/min; N₂/O₂: 0.3 mL/min; catalyst: 0.014 g; TON_S were calculated for t=447 min. Inlet operating pressure: 1.25 barg.

toluene as opposed to previous claims that toluene is formed by hydrogenolysis of benzyl alcohol [17,22].

3.2. Oxidation versus disproportionation of benzyl alcohol under aerobic conditions

From the data provided in Section 3.1 and from previous studies, further proof that disproportionation of benzyl alcohol reaction is the only reaction that is active under anaerobic conditions is provided. When an oxidant is used in this reaction, instead of He alone, besides disproportionation, oxidative dehydrogenation of benzyl alcohol to benzaldehyde occurs and in fact becomes the most favoured reaction. With the help of the new quantification methodology, it becomes easier to study the response of these two reactions separately to increases in temperature. Initially, the reactions were performed in a GSR at 80, 100 and 120 °C and the TON_O, TON_D and TON_{Tot} values are presented in Fig. 2A. With increase of temperature there is an overall increase in TON_{Tot}, mostly because of the higher contribution from TON_D as compared to TON_O. Besides toluene and benzaldehyde, other products including benzene, dibenzyl ether, benzoic acid and benzyl benzoate were also detected, but at very low concentrations (<5% molar selectivity). As the objective of this present work was to investigate these reactions in a continuous mode, the reactions were carried out in a MPBR at 80, 100, 120, 140 °C and the different turn-over numbers (TON_O, TON_D and TON_{Tot}) were calculated for all the runs. A pressure drop of 1.25 bar was also observed over the range of temperatures studied and did not vary significantly with the increase of temperature. The effect of temperature on the different turnover numbers is interesting as shown in Fig. 2B. Initially, an increase in oxidation was observed from 80 °C to 100 °C followed by a stabilisation at temperatures 120 °C and 140 °C. A substantial increase in the disproportionation reaction (TON_D) was observed with an increase in the reaction temperature. At reaction temperatures above 100 °C, any increase in the overall reaction (TON_{Tot}) is exclusively because of an increase in the disproportionation reaction and not the oxidation reaction. This suggests that raising the temperature is not the correct approach to increase the yield of the desired benzaldehyde product. This trend is more pronounced in MPBR when compared to GSR. At every temperature tested, TON_D is higher in the MPBR compared to the GSR. Stoichiometrically, oxygen is not involved in the disproportionation reaction, but comparing the TON_D data between aerobic and anaerobic conditions at different temperatures (Table 1), it is evident that oxygen has a substantial promotional effect on the disproportionation reaction. This observation in the MPBR is in agreement with the GSR [23].

3.3. Effect of reaction atmosphere

The oxidation of benzyl alcohol using 1%AuPdTiO₂ catalyst was examined further at different O₂ concentrations and O₂ pressures. The initial results from the GSR (Table 2) showed that the disproportionation reaction was promoted by increasing O₂ concentrations.

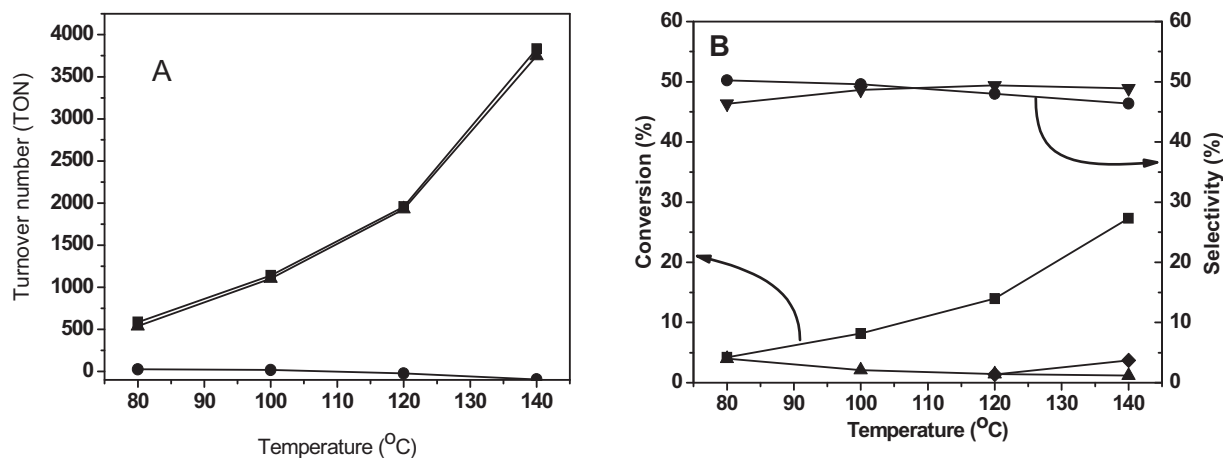


Fig. 1. Effect of temperature on disproportionation and oxidation reactions under anaerobic conditions in the MPBR. Reaction conditions: benzyl alcohol: 0.003 mL/min; N₂: 0.3 mL/min; 1%Au-Pd/TiO₂ catalyst: 0.014 g. TON_s were calculated for t = 447 min. Keys: (A) Turnover numbers data: oxidation turnover number (TON_O): ●, disproportionation turnover number (TON_D): ▲ and overall turnover number (TON_{Tot}): ■. (B) Conversion and selectivity data: benzyl alcohol conversion: ■, benzaldehyde selectivity: ●, toluene selectivity: ▼, benzene selectivity: ▲ and dibenzyl ether selectivity: ◆.

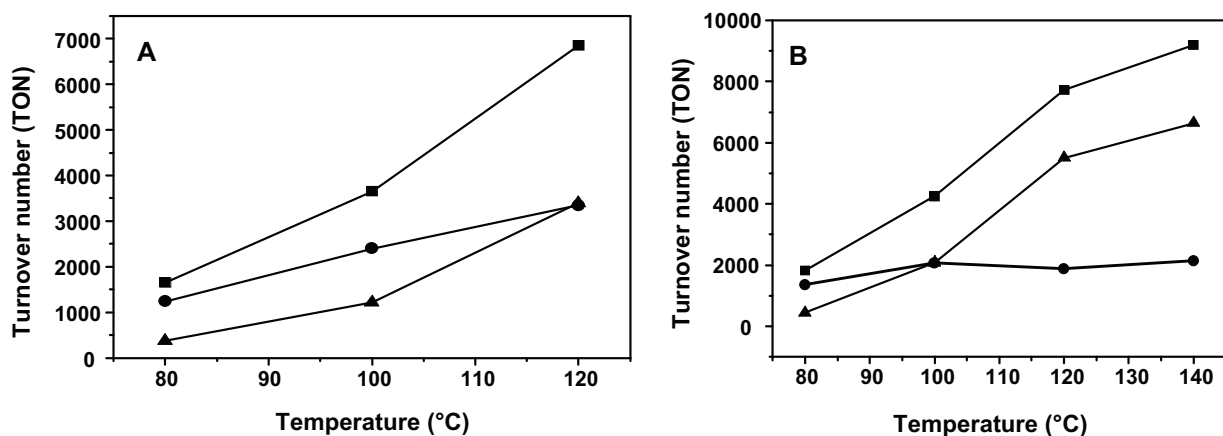


Fig. 2. Effect of temperature on disproportionation and oxidation reactions under aerobic conditions in the GSR (A) and MPBR (B). Reaction conditions: MPBR: benzyl alcohol: 0.003 mL/min; O₂: 0.3 mL/min; 1%AuPd/TiO₂ catalyst: 0.0026 g. TON_s were obtained for t = 83 min. GSR: benzyl alcohol: 2 g; 1%AuPd/TiO₂ catalyst: 0.02 g; pO₂: 1 barg; TON_s were obtained for t = 75 min. Keys: (A and B) Total TON: ■; oxidation TON: ●; disproportionation TON: ▲.

However, the TON_D reached a maximum in pure O₂ at 1 barg, and then decreased with further increase in O₂ pressure to 3 barg. In the MPBR, this TON_D decreasing trend was also observed at O₂ pressure extending to 4 barg (Table 3). It was also noted that the oxidation TON (TON_O) and the total TON (TON_{Tot}) increased monotonically with O₂ pressure within the pressure range studied. The dependence of TON_D on O₂ pressure suggests that there can be two different mechanisms for these disproportionation reactions, one anaerobic and the other promoted by oxygen; the complexity of the dependence arising from the interaction between the two disproportionation routes, at least when carried out on AuPd/TiO₂ catalysts.

3.4. Effect of catalyst support on disproportionation: GSR versus MPBR

Previously, we reported that MgO and ZnO supported gold palladium catalysts completely switched-off the disproportionation reaction, and thus toluene production in the GSR. We used the same catalyst, 1%AuPd/MgO, in an MPBR for the oxidation of benzyl alcohol under aerobic conditions in the temperature range of 80–140 °C; the results are listed in Table 4. With the increase in temperature, the alcohol conversion increased from 3.5% to 37.6%, but the selectivity to aldehyde and toluene remains constant without any substantial change. In contrast to observations in the GSR, in

Table 2
Effect of reaction atmosphere on TON_D, TON_O and TON_{Tot} in GSR.^a

Reaction atmosphere	Pressure (barg)	TON _D	TON _O	TON _{Tot}
He	1	814	116	1039
Air	1	1690	358	2095
O ₂	1	2230	1610	3903
O ₂	2	1660	1830	3544
O ₂	3	1440	2380	3866

^a Reaction conditions: benzyl alcohol: 2 g; 1%AuPd/TiO₂ catalyst: 0.02 g; temperature: 120 °C; time: 30 min.

Table 3
Effect of O₂ inlet pressure on TON_D, TON_O and TON_{Tot} in MPBR.^a

Pressure (barg)	TON _D	TON _O	TON _{Tot}
1.1	8493	2103	11009
2.1	8082	3887	12444
3.0	5524	6862	13325
4.0	4240	8307	13399

^a Reaction conditions: benzyl alcohol: 0.003 mL/min; O₂: 0.6 mL/min; 1%AuPd/TiO₂ catalyst: 0.0062 g; temperature: 120 °C. TON_s were calculated for t = 198 min.

Table 4
Effect of temperature on the reactivity of 1%AuPd/MgO catalyst in MPBR.^a

Reaction temperature (°C)	Conversion (%)	Products selectivity (%)				
		Aldehyde	Toluene	Benzene	Acid	Ester
80	3.5	93	3	4	0	0
100	8.3	94	3	3	0	0
120	22.6	93	3	1	1	2
140	37.6	91	4	2	1	2

^a Reaction conditions: catalyst: 0.006 g; benzyl alcohol: 0.003 mL/min; O₂: 0.6 mL/min; inlet operating pressure 0.68 barg.

the MPBR we observed a very small amount of toluene (ca. 3%) at all the temperatures studied. The MgO supported catalysts displayed lower activity compared to their TiO₂ analogues. At 120 °C, the 1%AuPd/TiO₂ catalyst resulted in approximately 50% conversion, whereas the 1%AuPd/MgO catalyst gave approximately 23% conversion, but with a substantial increase of benzaldehyde selectivity of around 60% for the TiO₂ supported catalyst to ~94% for the MgO supported catalyst. This is because the TiO₂ supported catalysts promote both oxidation and disproportionation reactions. Consequently, the overall higher activity for the TiO₂ supported catalyst is due to the additive contribution of both reactions, whereas the MgO supported catalyst only selectively promotes the oxidation reaction. Detailed quantitative studies performed in a GSR indicate that the interfacial sites between the nanoparticles and support play a crucial role in the disproportionation reaction [23]. By changing the support from TiO₂ to MgO there is a substantial decrease in the disproportionation reaction, and thus in toluene selectivity, both in GSR and MPBR. The reason for this observed difference between

the TiO₂ and MgO supported catalysts is speculated to be the mode of adsorption of the benzyl alcohol molecules at the metal–support interface for the disproportionation reaction. This difference in the mode of adsorption is attributed to the higher basicity of the MgO support [23].

3.5. Scanning transmission electron microscopy characterisation

Representative STEM-HAADF images and corresponding particle size distributions for the TiO₂ supported catalyst and the MgO supported catalyst are presented in Figs. 3 and 4A and B respectively. It is clear that there is no major difference in the metal particle size distributions for these two catalysts. This is hardly surprising as both these catalysts were derived from the same starting colloids which were subjected to an identical thermal history. Detailed higher resolution HAADF and XEDS studies indicated that the metal particles were Au–Pd alloys in both catalyst systems (Figs. 3 and 4C and D). Furthermore, on both supports, there is a

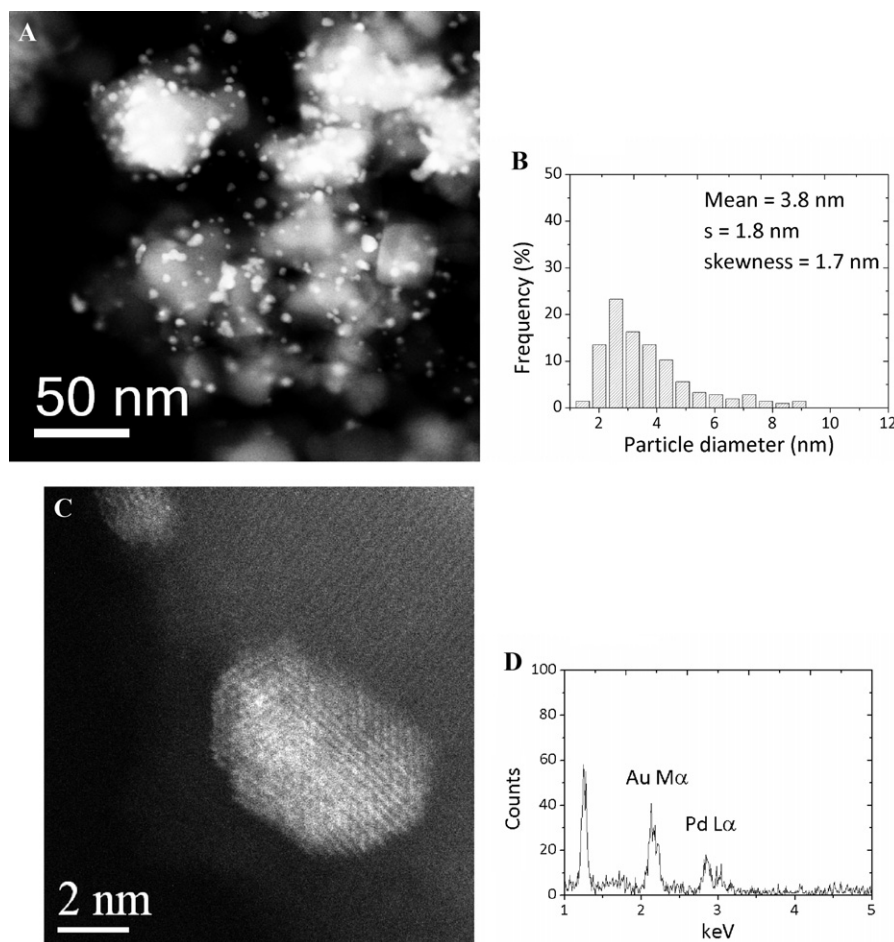


Fig. 3. (A) STEM-HAADF image and (B) corresponding particle size distribution for 1%AuPd/TiO₂ catalyst prepared by sol immobilization. (C) Atomic resolution HAADF image of a typical metal nanoparticle and (D) its corresponding XEDS spectrum confirming that it is an alloy of Au and Pd.

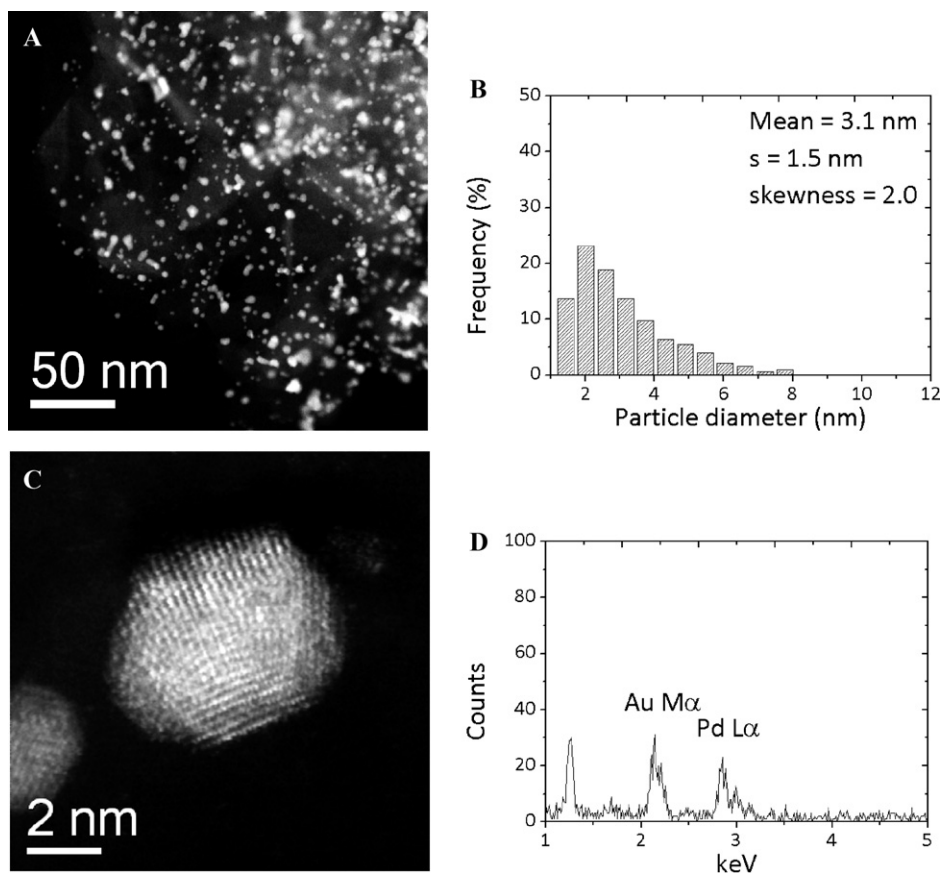


Fig. 4. (A) STEM-HAADF image and (B) corresponding particle size distribution for 1%AuPd/MgO catalyst prepared by sol immobilization. (C) Atomic resolution HAADF image of a typical individual metal nanoparticle and (D) its corresponding XEDS spectrum confirming that it is an alloy of Au and Pd.

tendency for the colloidal metal particles to wet the underlying oxide as evidenced by the particle flattening and surface faceting [23]. This intimate wetting contact creates a large number of interface sites and provides good anchoring of the alloy particle to the support. These electron microscopy results imply that the difference in promotional behaviour for the disproportionation reaction between these two catalysts is not simply due to any gross differences in AuPd nanoparticle size distribution, number density, morphology, composition and strength of metal interaction with the support. The difference in catalytic behaviour is much more subtle in origin and may be related to the redox behaviour or surface compositional characteristics of the oxide support.

4. Conclusion

The disproportionation of benzyl alcohol on a 1%AuPd/TiO₂ catalyst was confirmed experimentally in a micro-packed bed reactor under anaerobic conditions to produce equimolar amounts of benzaldehyde and toluene. The disproportionation reaction is promoted by increases in O₂ concentration/pressure up to 1 barg, but this promotion effect was reduced by further increases in O₂ pressure. This dependence of the disproportionation reaction on O₂ pressure may imply the existence of two mechanisms of disproportionation – one aerobic and the other anaerobic.

Acknowledgements

The authors acknowledge the EPSRC for funding. M.M. thanks Umm Al-Qura University, Saudi Arabia for the award of a Ph.D. studentship.

References

- [1] G. Cainelli, G. Cardillo, *Chromium Oxidations in Organic Chemistry*, Springer Verlag, Berlin, 1984.
- [2] R.A. Sheldon, J.K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981.
- [3] J.E. Bäckvall, *Modern Oxidation Methods*, Wiley-VCH, Weinheim, 2004.
- [4] T. Mallat, A. Baiker, *Chemical Reviews* 104 (2004) 3037.
- [5] C.D. Pina, E. Falletta, L. Prati, M. Rossi, *Chemical Society Reviews* 37 (2008) 2077.
- [6] A. Corma, H. García, *Chemical Society Reviews* 37 (2008) 2096.
- [7] N. Lopez, J.K. Nørskov, *Surface Science* 515 (2002) 175.
- [8] M. Casaletto, A. Longo, A. Venezia, A. Martorana, A. Prestianni, *Applied Catalysis A: General* 302 (2006) 309.
- [9] Z. Zhou, S. Kooi, M. Flytzani-Stephanopoulos, H. Saltsburg, *Advanced Functional Materials* 18 (2008) 2801.
- [10] A. Abad, P. Concepcion, A. Corma, H. García, *Angewandte Chemie International Edition* 117 (2005) 4134.
- [11] D.I. Enache, J.K. Edwards, P. Landon, B. Solsona-Espriu, A.F. Carley, A.A. Herzinger, M. Watanabe, C.J. Kiely, D.W. Knight, G.J. Hutchings, *Science* 311 (2006) 362.
- [12] S. Meenakshisundaram, E. Nowicka, P.J. Miedziak, G.L. Brett, R.L. Jenkins, N. Dimitratos, S.H. Taylor, D.W. Knight, D. Bethell, G.J. Hutchings, *Faraday Discussions* 145 (2010) 341.
- [13] L. Kesavan, R. Tiruvalam, M.H. Ab Rahim, M.I. bin Saiman, D.I. Enache, R.L. Jenkins, N. Dimitratos, J.A. Lopez-Sanchez, S.H. Taylor, D.W. Knight, C.J. Kiely, G.J. Hutchings, *Science* 311 (2011) 195.
- [14] A. Villa, N. Janjic, P. Spontoni, D. Wang, D.S. Su, L. Prati, *Applied Catalysis A: General* 364 (2009) 221.
- [15] K. Yamaguchi, N. Mizuno, *Angewandte Chemie International Edition* 114 (2002) 4538.
- [16] V.R. Choudhary, D.K. Dumbre, *Applied Catalysis A: General* 375 (2010) 252.
- [17] D. Ferri, C. Mondelli, F. Krumeich, A. Baiker, *Journal of Physical Chemistry B* 110 (2006) 22982.
- [18] E. Cao, M. Sankar, S. Firth, K.F. Lam, D. Bethell, D.K. Knight, G.J. Hutchings, P.F. McMillan, A. Gavriilidis, *Chemical Engineering Journal* 167 (2011) 734.
- [19] D.I. Enache, D.W. Knight, G.J. Hutchings, *Catalysis Letters* 103 (2005) 43.
- [20] S.S. Hladyi, M.K. Starchevsky, Y.A. Pazdersky, M.N. Vargaftik, I. Moiseev, *Mendeleeev Communications* 12 (2002) 45.
- [21] G. Kovtun, T. Kameneva, S. Hladyi, M. Starchevsky, Y. Pazdersky, I. Stolarov, M. Vargaftik, I. Moiseev, *Advanced Synthesis and Catalysis* 344 (2002) 957.

- [22] D.M. Meier, A. Urakawa, A. Baiker, *Journal of Physical Chemistry C* 113 (2009) 21849.
- [23] M. Sankar, E. Nowicka, R. Tiruvalam, Q. He, S.H. Taylor, C.J. Kiely, D. Bethell, D.W. Knight, G.J. Hutchings, *Chemistry: A European Journal* 17 (2011) 6524.
- [24] M.W. Losey, M.A. Schmidt, K.F. Jensen, *Industrial and Engineering Chemistry Research* 40 (2001) 2555.
- [25] V. Hessel, K.K. Yeong, A. Gavriilidis, R. Zapf, *Catalysis Today* 81 (2003) 641.
- [26] S. Tadepalli, R. Halder, A. Lawal, *Chemical Engineering Science* 62 (2007) 2663.
- [27] V. Hessel, A. Renken, J.C. Schouten, J. Yoshida, "Micro Process Engineering: A Comprehensive Handbook", Wiley-Blackwell, 2009.
- [28] N. Dimitratos, J.A. Lopez-Sanchez, D. Morgan, A.F. Carley, R. Tiruvalam, C.J. Kiely, D. Bethell, G.J. Hutchings, *Physical Chemistry Chemical Physics* 11 (2009) 5142.
- [29] R.C. Tiruvalam, J.C. Pritchard, N. Dimitratos, J.A. Lopez-Sanchez, J.K. Edwards, A.F. Carley, G.J. Hutchings, C.J. Kiely, *Faraday Discussions* 152 (2011) 63.