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Controlling the Duality of the Mechanism in Liquid-Phase Oxidation of Benzyl Alcohol Catalysed by Supported Au–Pd Nanoparticles

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Abstract: In the solvent-free oxidation of benzyl alcohol to benzaldehyde using supported gold–palladium nanoparticles as catalysts, two pathways have been identified as the sources of the principal product, benzaldehyde. One is the direct catalytic oxidation of benzyl alcohol to benzaldehyde by O₂, whereas the second is the disproportionation of two molecules of benzyl alco-

hol to give equal amounts of benzaldehyde and toluene. Herein we report that by changing the metal oxide used to support the metal–nanoparticles catalyst from titania or niobium oxide to

Keywords: basicity/acidity • disproportionation • gold–palladium nanoparticles • oxidation • support effect

magnesium oxide or zinc oxide, it is possible to switch off the disproportionation reaction and thereby completely stop the toluene formation. It has been observed that the presence of O₂ increases the turnover number of this disproportionation reaction as compared to reactions in a helium atmosphere, implying that there are two catalytic pathways leading to toluene.

Introduction

Interest in catalysis by supported gold and gold–palladium nanoparticles has undergone a tremendous resurgence because of its great potential in the development of environmentally benign processes. Following the discoveries by Haruta and Hutchings in the use of gold nanoparticles as catalysts for the oxidation of CO and ethyne hydrochlorination respectively in the 1980s, interest in catalysis by supported gold and gold–palladium nanoparticles has expanded dramatically.^[1] This has led to the discoveries of gold and gold palladium based catalysts for the direct synthesis of H₂O₂ from H₂ and O₂,^[2] epoxidation of alkenes^[3] and oxidation of alcohols^[4] and polyols.^[5]

Oxidation is a fundamental functional-group transformation in general organic synthesis.^[6] It often shows a number of undesirable features, such as the requirement for relatively expensive and toxic stoichiometric reagents, less than perfect yields, and sometimes complicated product-separation procedures.^[7] This is well illustrated when one considers ap-

plications of well-established oxidants based on manganese and chromium.^[8] Many modern oxidising reagents such as the Swern method, *o*-iodoxybenzoic acid (IBX), Dess–Martin periodinane and tetrapropylammonium perruthenate (TPAP), rapidly gained general acceptance as ‘standard’ reagents because of their outstanding ability as clean oxidants with respect to product formation rather than any significant positive cost, scale-up or environmental features. Indeed, their adoption was often in spite of these latter considerations.^[8] Clearly, one aspiration in this area is to define oxidants and catalyst systems which operate as efficiently and as benignly as do hydrogenation catalysts, widely employed for example in the reduction of alkenes to alkanes.^[9] For the stoichiometric oxidant, the obvious green candidate is molecular oxygen (air) or derived hydrogen peroxide,^[10] while both supported gold and palladium nanoparticles show considerable promise as recyclable heterogeneous catalysts in this area, a combination which offers tremendous potential in terms of general environmental friendliness.^[2–5]

Selectivity and mechanism are features of this new science which must be understood to assist catalyst design and fine tuning. To achieve very high selectivity in a particular reaction, it is important to understand all the parallel and consecutive reactions that are active in the overall transformation, which can lead to side-products and thus a lower selectivity for the product of interest.^[11,12] Among the alcohols, benzyl alcohol is one of the most studied examples for the selective oxidation to aldehydes.^[12] Benzyl alcohol undergoes a variety of reactions depending on the reaction conditions and the nature of the catalyst used. The reactions reported so far are a) oxidation to form benzaldehyde, benzoic acid and benzyl benzoate,^[13] b) disproportionation to form benzaldehyde, toluene and water,^[14] c) dehydration to form

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dibenzylether,^[15] and d) self-condensation (benzylation) to form anthracene and stilbene.^[16] Many reactions are active only under particular reaction conditions; for example, condensation to form anthracene and stilbene are found to be active at higher temperatures in the vapour phase.^[16] In the low temperature liquid-phase oxidation of benzyl alcohol, depending on the reaction conditions and catalysts used, many products including benzoic acid, benzyl benzoate, dibenzyl ether and toluene have been reported to be formed besides the main product benzaldehyde.^[17] A clear understanding of the mechanism of the formation of all these products is necessary to fine-tune the catalyst for the selective formation of the desired product, benzaldehyde. It has been generally accepted that benzaldehyde forms by the oxidation of benzyl alcohol in the presence of an oxidant; benzaldehyde on further oxidation then leads to the formation of benzoic acid and the next product, benzyl benzoate, is formed either by the reaction between benzoic acid and benzyl alcohol or by the oxidation of a hemiacetal.^[17] Toluene is the other major product; its origin is still under debate.^[14,18,19] In an earlier report in which roughly equimolar amounts of toluene and benzaldehyde were produced from benzyl alcohol using Au–Pd catalysts in a helium atmosphere, we proposed a disproportionation of two moles of benzyl alcohol to be the origin of toluene as shown in Scheme 1.^[14]



Scheme 1. Disproportionation of two moles of benzyl alcohol leading to equimolar amounts of toluene and benzaldehyde.

This reaction is feasible because of the slightly negative overall enthalpy of the reaction. Herein, we further investigate the origin and catalytic sites responsible for the disproportionation reaction, and finally demonstrate how to “switch off” this reaction by fine-tuning the catalyst.

Results and Discussion

Quantitative separation of two reactions: The solvent-free oxidation of benzyl alcohol was carried out at 393 K using a 1 % (Au–Pd)/TiO₂ catalyst, prepared by a sol-immobilisation method, under 1 bar O₂ (relative) pressure. Reaction mixtures extracted at periodic time intervals were analysed quantitatively by using gas chromatography (GC). Figure 1 shows the representative time online profile of the benzyl alcohol conversion and the selectivity towards the major products. Initially, benzyl alcohol conversion increases steeply and then reaches a near plateau at approximately 70 mol% conversion. The product mixture, at all times, comprises benzaldehyde (ca. 75 %), toluene (ca. 23–24 %) and a minor amount of benzoic acid. The other possible products, namely benzene, benzyl benzoate and dibenzyl ether are either observed at a trace level of less than 0.5 % or are not observed at all under our experimental condi-

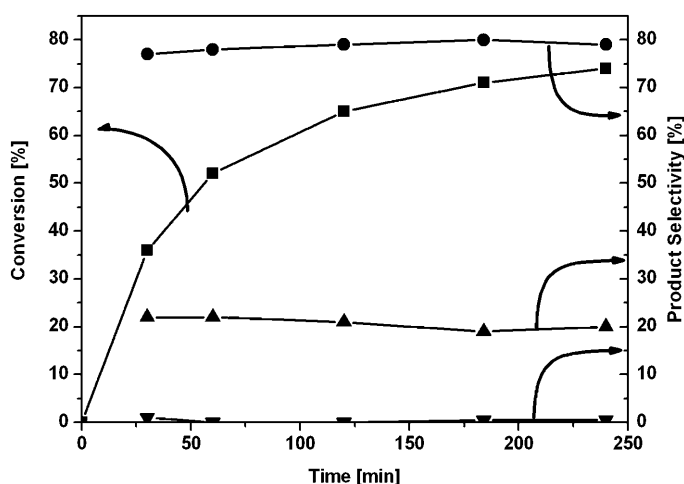


Figure 1. Oxidation of benzyl alcohol using 1 % (Au–Pd)/TiO₂ under 1 bar O₂ (relative) pressure at 393 K; substrate to metal molar ratio: 14000; benzyl alcohol: 18.5 mmol. ■: Benzylalcohol molar conversion, ●: benzaldehyde selectivity; ▲: toluene selectivity; ▼: benzoic acid selectivity.

tions. For simplicity, the selectivity data for benzyl benzoate, benzene and dibenzyl ether, whenever they are formed, have not been included in Figure 1.

Benzaldehyde, the major product, is formed by the oxidation of benzyl alcohol, and toluene and benzaldehyde are formed by the disproportionation of benzyl alcohol. Therefore, there are two active reactions in the overall oxidation of benzyl alcohol. Herein, we attempt to quantify these two reactions separately and try to understand the effect of the nature of the catalyst and the reaction parameters on these two reactions separately. The separation and quantification of these two reactions has been performed using the following underlying premise. Benzaldehyde is formed from the disproportionation and the oxidation reactions, so it cannot be used to quantify either reaction. However, toluene is formed exclusively from disproportionation; therefore the amount of toluene formed can be used as a measure of the extent of the disproportionation reaction. According to Scheme 1, the number of moles of benzyl alcohol consumed in disproportionation is twice the number of moles of toluene formed. From this value, a disproportionation turnover number (TON_D) was calculated using Equation (1).

$$\text{TON}_D = 2 \times \text{mol}_{\text{Tol}} / \text{mol}_{\text{Metal}} \quad (1)$$

TON_D is used to represent the disproportionation reaction quantitatively in this paper. Benzaldehyde is formed from both the reactions; the moles of benzaldehyde formed by disproportionation is equal to the number of moles of toluene formed. By subtraction, the moles of benzaldehyde formed by the oxidation reaction can then be calculated and converted into an oxidation turnover number (TON_O) using Equation (2).

$$\text{TON}_O = (\text{mol}_{\text{BCHO}} - \text{mol}_{\text{Tol}}) / \text{mol}_{\text{Metal}} \quad (2)$$

The TON_O parameter is used for the quantitative representation of the oxidation reaction in this paper. Using Equations (1) and (2), TON_O and TON_D values were calculated for all the points in Figure 1 and are presented in Figure 2. The TON_Tot represents the overall reaction, calculated from the moles of benzyl alcohol consumed and the moles of the metals contained in the catalyst.

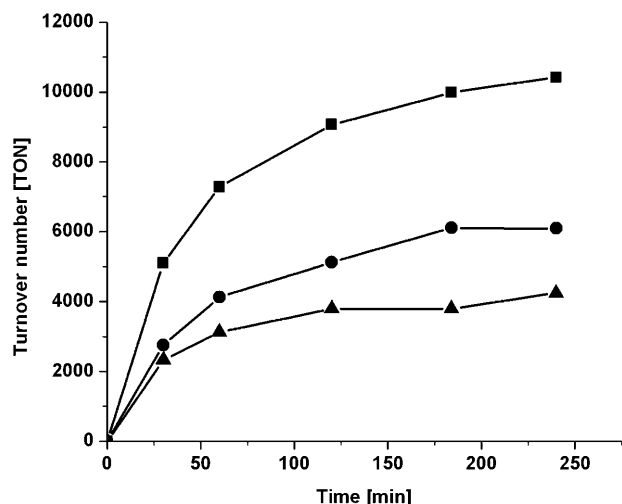


Figure 2. Time profile of the turnover numbers (TON_D and TON_O) corresponding to the oxidation and disproportionation reactions respectively in the oxidation of benzyl alcohol using 1% (Au-Pd)/ TiO_2 under 1 bar (relative) O_2 pressure at 393 K; substrate versus metal molar ratio: 14000; benzyl alcohol: 18.5 mmol. ■: TON_Tot ; ●: TON_O ; ▲: TON_D .

After separating the two processes analytically, our next aim was to separate these two processes experimentally. By removing the oxidant, the oxidation reaction was suppressed thereby forcing the system to undergo disproportionation exclusively.^[14,19] To study the disproportionation reaction alone, benzyl alcohol was treated with a 1% (Au-Pd)/ TiO_2 catalyst under similar conditions to the previous experiments, except that 1 bar He was used instead of 1 bar O_2 to create an inert atmosphere. The turnover numbers for the oxidation reaction, disproportionation reaction and the overall reaction for this inert situation are plotted in Figure 3.

From the results, we see that the TON_Tot is very close to the TON_D ; disproportionation is the only active reaction under these conditions. Quantitative GC analyses of the product mixtures show that benzaldehyde and toluene are formed exclusively. The molar ratio of benzaldehyde to toluene is slightly higher than unity. This slight excess of benzaldehyde is because of oxidation by O_2 adsorbed on the surface of the catalysts, which could not be removed. From Figure 3, it is evident that there is no significant increase in the oxidation reaction TON_O with time after the first 30 minutes. This is because, after the consumption of the trace of available residual adsorbed O_2 in the system, the oxidation switches off automatically. It should be noted that this result indicates that benzaldehyde is not being produced by a dehydrogenation pathway ($\text{PhCH}_2\text{OH} \rightarrow \text{PhCHO} + \text{H}_2$) in these

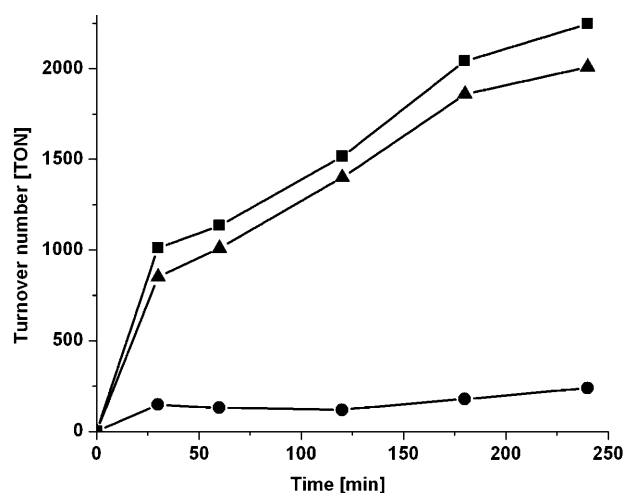


Figure 3. Time profiles of TON_Tot , TON_O and TON_D in the reaction of benzyl alcohol using 1% (Au-Pd)/ TiO_2 at 393 K under 1 bar (relative) He pressure; substrate versus metal molar ratio: 14000; benzyl alcohol: 18.5 mmol. ■: TON_Tot ; ●: TON_O ; ▲: TON_D .

systems. In another report by Hladyi et al. for the same reaction, a homogeneous Pd cluster catalyst was purged with He to achieve the 100% inert condition, and the authors could achieve exactly the same amount of benzaldehyde and toluene.^[19] In the present work, since the catalyst used was a solid metal oxide supported catalyst, the adsorbed O_2 could not be removed completely in our experimental procedure using the glass reactor, but by using a more efficient micro-bed reactor, using the same catalyst, we have achieved the complete removal of O_2 and hence we have been able to study the disproportionation reaction under anaerobic conditions.^[20] This demonstrates that this is a disproportionation of benzyl alcohol to benzaldehyde and toluene in exactly equal quantities.

Effect of reaction parameters on the disproportionation reaction: To study this aspect, benzyl alcohol reactions were performed using a 1% (Au-Pd)/ TiO_2 catalyst under either O_2 or He atmospheres at different temperatures, that is, 353, 373 and 393 K. The TON_D values for all these experiments are shown in Table 1. From the data reported in Table 1, it is clear that with a rise in temperature from 353 to 393 K there is an increase in the disproportionation TON from 455 to 1010. Another interesting result is the comparison of the disproportionation TON, at any given temperature, under He and O_2 atmospheres. At 393 K, the disproportionation

Table 1. Effect of temperature and the reaction atmosphere on the turnover numbers.^[a]

T [K]	TON_D (under He)	TON_D (under O_2)	TON_O
353	455	1180	2920
373	791	2220	5070
393	2010	4250	6090

[a] Reaction conditions: Catalyst: 1% (Au-Pd)/ TiO_2 ; substrate: 18.5 mmol; substrate versus metal molar ratio: 14000; He or O_2 pressure: 1 bar (relative), time: 4 h.

TON under He is 2010 whereas under O₂ it is 4250. This shows that O₂ promotes the disproportionation reaction. This enhancement is apparent at 353 and 373 K as well but with lesser turnover numbers. Thus, lower temperatures do not favour the disproportionation reaction and hence the formation of toluene.

Active site for the disproportionation reaction: Au or Pd or Au–Pd? To determine the active sites responsible for the disproportionation reaction, two monometallic catalysts, 1 % Au/TiO₂ and 1 % Pd/TiO₂, were prepared using the same sol-immobilisation technique. The benzyl alcohol reaction was carried out using 1 % Au/TiO₂ as catalyst at 393 K under 1 bar (relative) O₂ pressure. Samples were analysed at regular intervals and the turnover numbers for the reaction were calculated. The data for the Au/TiO₂ catalysts is shown in Table 2 from which it is apparent that the pure Au catalyst

Table 2. Turnover numbers for the oxidation and disproportionation reactions in the reaction of benzyl alcohol using 1 % Au/TiO₂ catalyst.^[a]

Time [min]	Under O ₂			Under He		
	TON _O	TON _D	TON _{Tot}	TON _O	TON _D	TON _{Tot}
30	98	0.06	103	7.0	0.1	7.1
120	137	0	137	7.3	0.2	7.5
180	169	0	169	7.4	0.3	8

[a] Reaction conditions: Substrate: 18.5 mmol; substrate versus metal molar ratio: 14000; temperature : 393 K; O₂ or He Pressure: 1 bar (relative).

is not nearly as active as the corresponding Au–Pd catalyst. The total turnover number for the Au–Pd catalyst, after 184 min, was 9989, but for the Au catalyst this was 169 after 180 minutes. A second important observation is that the TON_{Tot} value obtained for the monometallic Au catalyst, equals the TON_O value and so the TON_D was effectively zero. Evidently the pure Au sites do not catalyse the disproportionation reaction.

To confirm this postulate, the benzyl alcohol reaction was carried out under 1 bar (relative) He pressure. The turnover numbers calculated are given in Table 2. The TON_{Tot} reduces to 7–8 and it stays constant throughout the reaction time. Again, oxidation by residual oxygen was the only reaction observed under these conditions. The TON_D is zero throughout the reaction. Thus, when the reaction conditions prevent oxidation and therefore enforce disproportionation, nanoparticles of pure gold do not catalyse the reaction. The 1 % Pd/TiO₂ sample was used to catalyse the oxidation of benzyl alcohol under 1 bar (relative) O₂ pressure at 393 K. The resulting turnover numbers are plotted in Figure 4. The pure Pd catalyst clearly promotes both oxidation and disproportionation, but the two reactions show lengthy but different induction periods. The oxidation appears to start after a shorter induction period (ca. 20 mins) than is required for the disproportionation reaction. Kaneda and co-workers have attributed the existence of these initial induction periods to the physical re-structuring of the catalyst from the as-

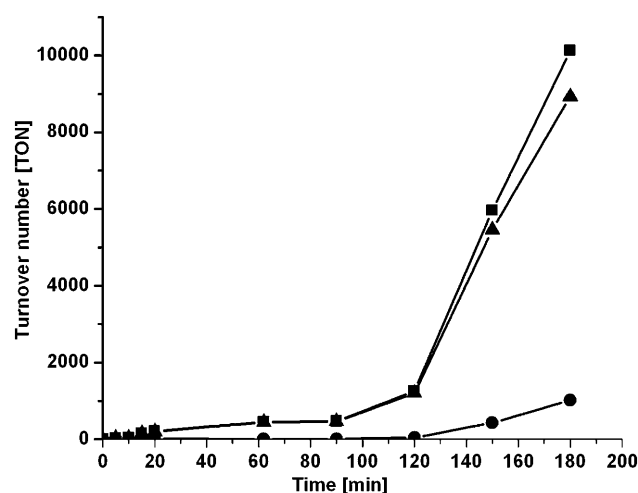


Figure 4. Time profile of the turnover numbers corresponding to the oxidation and disproportionation reactions in the reaction of benzyl alcohol using 1 % Pd/TiO₂ under 1 bar (relative) O₂ pressure at 393 K, substrate versus metal molar ratio: 14000; benzyl alcohol: 18.5 mmol. ■: TON_{Tot}; ●: TON_D; ▲: TON_O.

synthesized form to an active form.^[21] An interesting feature of this plot is the occurrence of a second induction period for the disproportionation reaction, which is much longer (ca. 120 min) than the overall induction period; up until this point, the overall turnover number TON_D is very close to the oxidation turnover number TON_O. These induction periods disappeared when Au was added to the Pd catalysts as evidenced in Figure 2. It has been reported that Ru or Ag based catalysts are capable of dehydrogenating benzyl alcohol in the absence of any oxidant.^[22] The catalysts reported here are not capable of dehydrogenating benzyl alcohol in the absence of oxidant; instead they induce disproportionation to form an equimolar mixture of benzaldehyde and toluene. It is important to note that, in the above mentioned reports, toluene was used as the solvent for the dehydrogenation of benzyl alcohol.^[22]

From these results, we can conclude that, in the reaction of benzyl alcohol, Au sites do not catalyse the disproportionation reaction and therefore do not cause any toluene formation. However, the pure Au catalyst is not sufficiently active to give an acceptable overall turnover number. By adding Pd to Au, the overall turnover number is significantly increased and, at the same time, the disproportionation reaction is switched on, forming toluene as a by-product. The key challenge is therefore to maintain the activity while at the same time switching off the disproportionation reaction.

Effect of different support materials: For this purpose, Au–Pd nanoparticles were supported on a variety of different supports including Nb₂O₅, activated C (G-60), MgO and ZnO. These catalysts were prepared using the same sol-immobilisation technique as described previously. Benzyl alcohol oxidation was carried out using all these catalysts under 1 bar (relative) O₂ pressure at 393 K. Samples were with-

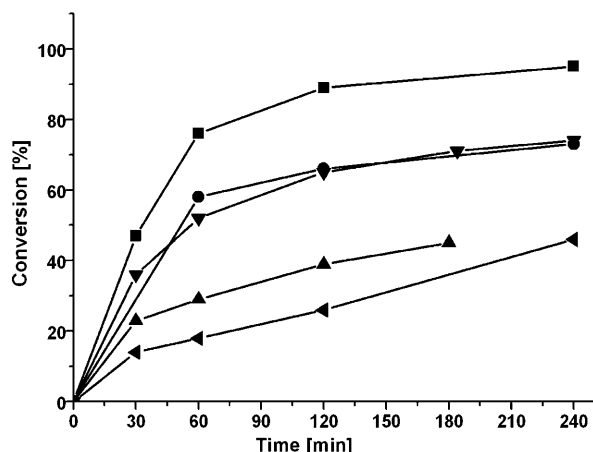


Figure 5. Kinetic profile for the oxidation of benzyl alcohol using different supported Au-Pd catalysts under 1 bar (relative) O_2 at 393 K; substrate versus metal molar ratio: 14000; Benzyl alcohol: 18.5 mmol. ■: 1% (Au-Pd)/C; ▲: 1% (Au-Pd)/ZnO; ▼: 1% (Au-Pd)/TiO₂; ◆: 1% (Au-Pd)/MgO; ●: 1% (Au-Pd)/Nb₂O₅.

drawn at regular intervals and analysed. The resultant kinetic plot is shown in Figure 5. The data indicates that Au-Pd supported on activated C (G-60) is the most active catalyst followed by the TiO₂ and Nb₂O₅-supported catalysts. The MgO- and ZnO-supported catalysts exhibited the least activity for the reaction. However, the selectivity data for these five catalysts are very different. Activated C-, TiO₂- and Nb₂O₅-supported catalysts formed toluene as a major by-product, whereas MgO- and ZnO-supported catalysts did not produce any toluene. For these latter two catalysts, benzaldehyde was the only major product with selectivity in excess of 99%. Hence, we can deduce that the MgO- and ZnO-supported catalysts switch off the disproportionation reaction and hence any toluene formation whereas the activated C, Nb₂O₅ and TiO₂ catalysts catalyse the disproportionation reaction. Interestingly, the sub-set of catalysts that catalyse disproportionation shows a higher overall activity. Hence, by simply changing the catalyst support, we can either switch on or switch off the disproportionation reaction. The turnover numbers for the oxidation and disproportionation reactions has been calculated for all these catalysts on different supports (Figures 6 and 7).

Surprisingly, the TON_O values for all these reactions were found to be more or less equivalent, with only very small deviations. This implies that the oxidation reaction is effectively independent of the identity of the support. However, the interesting feature for the MgO- or ZnO-supported catalysts is that they selectively catalyse the oxidation reaction and thus gives a >99% selectivity towards benzaldehyde. There is a clear difference in the activity for the disproportionation reaction for the differently supported AuPd catalysts. Activated-C-supported catalysts are found to be very active for the disproportionation reaction followed by TiO₂- and Nb₂O₅-supported catalysts. However, ZnO- and MgO-supported catalysts did not show any significant activity for the disproportionation reaction. This trend follows the overall

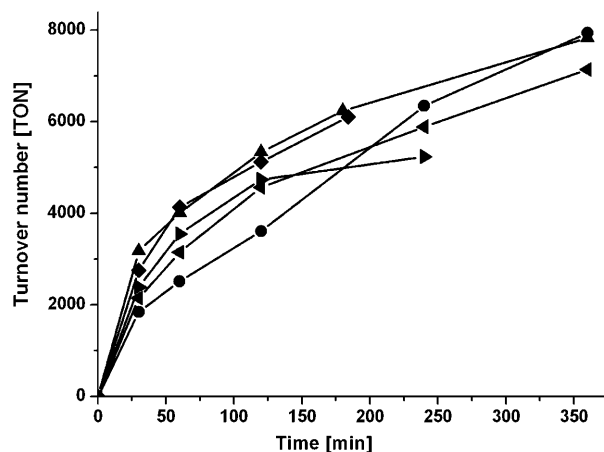


Figure 6. Time profile of the TON_O calculated for the oxidation of benzyl alcohol using different catalysts at 393 K under 1 bar (relative) O_2 substrate versus metal molar ratio: 14000; Benzyl alcohol: 18.5 mmol. ◆: 1% (Au-Pd)/TiO₂; ▲: 1% (Au-Pd)/ZnO; ●: 1% (Au-Pd)/MgO; ▼: 1% (Au-Pd)/Nb₂O₅; ►: 1% (Au-Pd)/C.

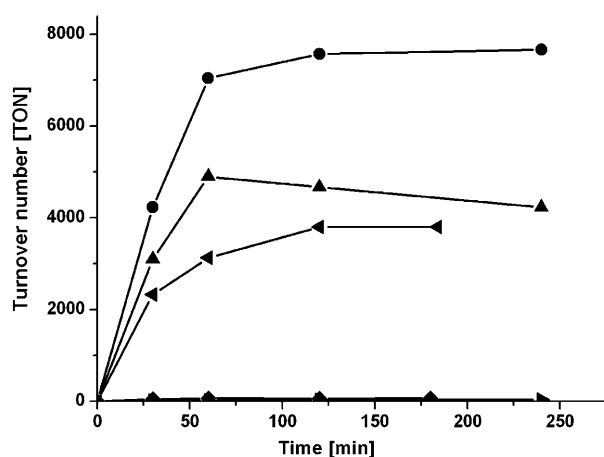


Figure 7. Time profile of the TON_D number calculated for the oxidation of benzyl alcohol using different catalysts at 393 K under 1 bar (relative) O_2 ; substrate versus metal molar ratio: 14000; Benzyl alcohol: 18.5 mmol. ■: 1% (Au-Pd)/ZnO; ▲: 1% (Au-Pd)/Nb₂O₅; ▼: 1% (Au-Pd)/MgO; ◆: 1% (Au-Pd)/TiO₂; ●: 1% (Au-Pd)/C.

activity trend, (i.e. activated C > Nb₂O₅ = TiO₂ > ZnO = MgO), as shown in Figure 5. By comparing the data in Figures 5–7 we conclude that the increased activity is due to the difference in the activity for the disproportionation reaction and not because of the oxidation reaction. From Table 2, we also know that the reaction atmosphere (i.e., O_2 or He) affects the activity for the disproportionation reaction. We therefore extended the atmosphere dependence study to the sub-set of catalysts which show activity for the disproportionation reaction. For this study, benzyl alcohol reactions were performed at 393 K using different catalysts for 4 hours under He atmosphere to force the system to undergo solely the disproportionation reaction. The TON_D values for these particular catalysts are presented in Table 3. For all the three catalysts under He, the TON_D values are

Table 3. Effect of support and reaction atmosphere on the TON_D.^[a]

Catalyst	TON _D under He	TON _D under O ₂
1 % (Au–Pd)/TiO ₂	2010	4250
1 % (Au–Pd)/Nb ₂ O ₅	1390	4230
1 % (Au–Pd)/C	1640	7800

[a] Reaction conditions: Substrate: 18.5 mmol; substrate versus metal molar ratio: 14000; He or O₂ pressure : 1 bar (relative); time: 4 h; temperature: 393 K.

rather similar. The corresponding TON_D values for the same materials were calculated under O₂ (Table 3). These show a remarkable difference in the activities for the disproportionation reaction between the activated-C-supported catalyst and those supported on TiO₂ and Nb₂O₅. The activated-C-supported catalyst showed a TON_D of 7800 whereas, the TiO₂-supported catalyst has a TON_D of 4250. The disproportionation reaction for the benzyl alcohol oxidation under O₂ atmosphere is therefore sensitive to the support and the active centre for this reaction could be at the interface between the bimetallic nanoparticles and the support. Hence, the shape and mode of attachment of the metal nanoparticles may be important parameters for controlling the disproportionation reaction.

Microscopy results: To investigate if the differences in the support materials affect the Au–Pd particle-size distribution or the mode of attachment of the metal nanoparticle to the metal oxide support, the catalysts were characterised initially by TEM and then by STEM. Representative bright field TEM images for all the catalysts along with their particle-size distributions are presented in Figure 8. From the particle-size distribution data, it is clear that there is no major difference between the primary Au–Pd bimetallic particle sizes on different supports, which mainly fall in the 3.0 to 6.0 nm size range. This is to be expected as all the metal particles were derived from the same AuPd colloid preparation. However, there is a distinct tendency for some of the metal particles on the MgO and ZnO (and to a much lesser extent TiO₂) supports to show some evidence of particle coalescence at the 120 °C drying temperature, giving rise to occasional particles that are greater than 10 nm in projected size. In contrast, none of the particles on the activated C and Nb₂O₅ supports, and only very few of them on the TiO₂ support, showed any signs of such coarsening. These slight differences in overall particle-size distribution probably do not account for the observed change in disproportionation catalytic behaviour when the support was changed from TiO₂, C or Nb₂O₅ to MgO or ZnO. Representative high angle annular dark field (HAADF) images obtained during our STEM analyses are shown in Figure 9. Detailed STEM data for the 1 % (Au–Pd)/TiO₂ and 1 % (Au–Pd)/C catalysts are reported elsewhere.^[23] Herein, we present STEM data for all the five catalysts. On MgO, ZnO and TiO₂ the AuPd nanoparticles have a tendency to wet the support as evidenced by particle flattening and surface faceting, as well as the development of an extended intimate particle/support interface. In direct contrast, no such wetting occurs on the Nb₂O₅ and activated

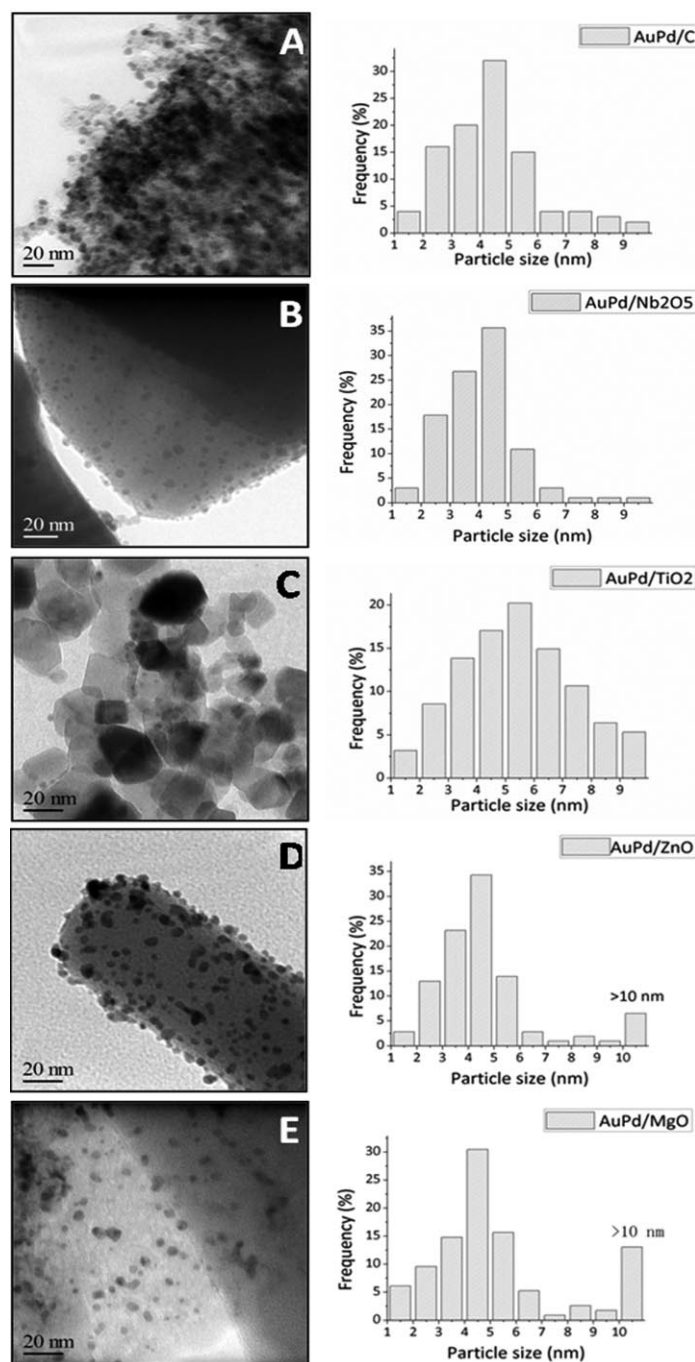


Figure 8. Particle-size distribution data, as determined from bright field TEM micrographs for the supported Au–Pd catalysts A) 1 % (Au–Pd)/C, B) 1 % (Au–Pd)/Nb₂O₅, C) 1 % (Au–Pd)/TiO₂, D) 1 % (Au–Pd)/ZnO and E) 1 % (Au–Pd)/MgO.

C supports where the AuPd particles retain a roughly spherical shape. Among the five different catalysts tested, the activity for the disproportionation reaction follows the trend, activated C > Nb₂O₅ > TiO₂ > MgO = ZnO. It is interesting to note that the tendency of the AuPd particles to wet the support material and undergo some degree of sintering at 120 °C follows the exact opposite trend (i.e., MgO = ZnO > TiO₂ > Nb₂O₅ > activated C).

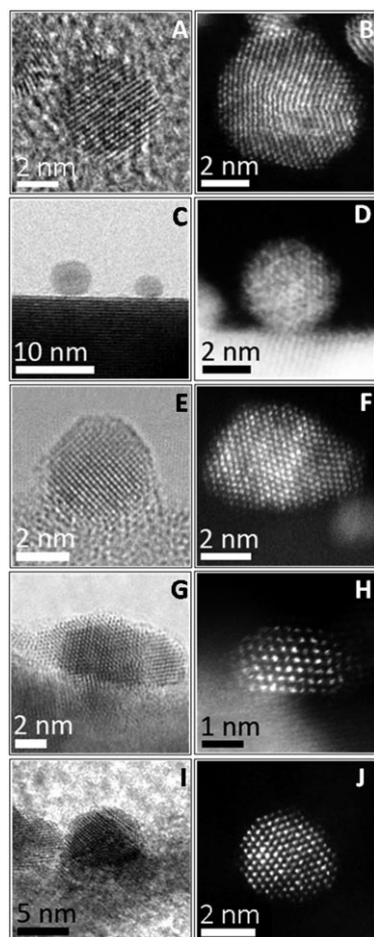


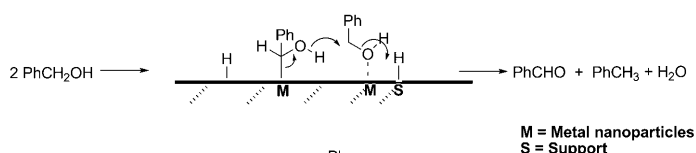
Figure 9. Pairs of HREM images (left) and STEM images (right) of the catalysts (A and B): 1% (Au-Pd)/C; (C and D): 1% (Au-Pd)/Nb₂O₅; (E and F): 1% (Au-Pd)/TiO₂; (G and H): 1% (Au-Pd)/ZnO and (I and J): 1% (Au-Pd)/MgO.

Comments on the mechanism: The observation by ourselves and others that, under non-oxidative conditions, benzyl alcohol can be transformed into an exactly equimolar mixture of benzaldehyde and toluene points to a disproportionation mechanism in which both products arise from a single transition state derived, by involvement of the catalyst surface, from two molecules of the alcohol.^[14,19] Separate pathways to toluene and benzaldehyde in the absence of oxygen would require an inconceivable coincidence of reaction rates. Under these anaerobic condition, when MgO- and ZnO-supported catalysts were used, there was little or no conversion of benzyl alcohol to either benzaldehyde or toluene.^[14] Our microscopy results on the Au-Pd particles on different supports offer no evidence of large differences in their physical appearance that would explain why there is such variability in the efficiency of catalysis of disproportionation; this points to a more chemical interpretation. Under oxidative conditions using 1% AuPd/TiO₂ catalyst, when a small amount of NaOH (0.5 wt% relative to the substrate) was added to the reaction mixture at the start of the reaction, the product mixture did not contain any toluene.

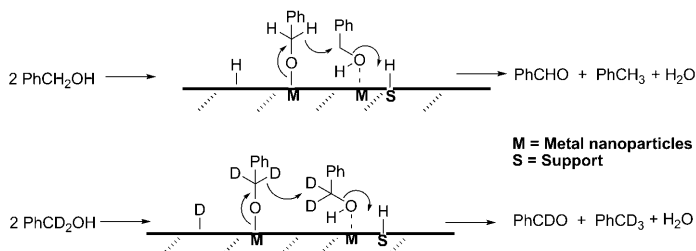
This suppression of toluene formation even with TiO₂-supported catalyst in the presence of a base indicates that the acidity/basicity of the reaction mixture or the catalytic surface plays a crucial role in controlling catalysis of the disproportionation reaction.

The generation of toluene necessarily involves cleavage of the C–O bond of benzyl alcohol and, by analogy with carbocation chemistry, this is likely to be promoted in acidic environments and inhibited under basic conditions, where O–H cleavage might be expected to be preferred. That toluene formation by disproportionation is favoured when Au–Pd particles are supported on acidic materials and does not occur at all when basic supports are used fits into this simple view. It seems therefore possible that the relevant catalytic sites are located close to the periphery of the metal particles where the metal and support surfaces are in intimate contact. This may lead to different modes of dissociative chemisorption of benzyl alcohol on the metal surface: 1) by cleavage of a benzylic C–H bond; 2) by cleavage of the O–H bond and 3) by cleavage of the benzylic C–O bond. We suggest that the presence of an acidic support increases the probability of attachment of PhCH₂-groups to the metal surface, as implied in Scheme 2. In our earlier study on the disproportionation reaction, using PhCD₂OH, we observed the formation of a mixture of PhCD₃ and PhCD₂H.^[14] To account for these two types of product, we propose two mechanistic pathways for toluene formation, involving H transfer from benzyl alcohol chemisorbed in two different ways to an adsorbed or incipient benzyl moiety. These mechanisms are shown in Scheme 2 and Scheme 3.

The role that oxygen plays in accelerating the disproportionation reaction remains a problem. One possible explanation could be that the presence of O₂ could help in the re-



Scheme 2. Dissociative chemisorption of benzyl alcohol on the metal-support surface. Mechanism for toluene formation.



Scheme 3. Dissociative chemisorption of benzyl alcohol on the metal-support surface. Mechanism for toluene formation.

generation of active sites for the disproportionation reaction by removing the adsorbed products of the disproportionation reaction. In an effort to understand the effect, the TON_D data at the end of 30 minutes of reaction, for the conditions mentioned in Table 3, were plotted logarithmically against $1/T$ (data not given). The plots were found to be linear and their slopes (apparent E_act) were calculated; the values for $\text{TON}_\text{D}(\text{He})$, $\text{TON}_\text{D}(\text{O}_2)$ and TON_O are 56.5, 99.8 and 51.5 kJ mol^{-1} respectively. This suggests that disproportionation under He and O_2 are quite different mechanistically. Further investigation is in progress.

In an atmosphere of oxygen, benzaldehyde formation becomes much more rapid. Since we have ruled out a dehydrogenation pathway by our experiments under helium, our earlier recognition that increasing oxygen availability leads to saturation kinetics indicates that a surface oxygen species is involved in removal of hydrogen from chemisorbed benzyl alcohol. This reaction is remarkably insensitive to the support used for the metal particles and this suggests that the catalytic sites are located on the metal away from the periphery of the particle and the surface of the support.

The synergy between gold and palladium that we have observed deserves a comment. Gold alone catalyses oxidation but not very effectively; it seems to be inactive in promoting disproportionation. Palladium nanoparticles are more effective for both processes but only after an extended induction period, which is longer for toluene formation than oxidation. The Au–Pd combination is even more catalytically active for both oxidation and disproportionation and there is no induction period. There appears to be no organic chemical reason for this pattern of behaviour. Further, more detailed electron microscopy seems likely to be necessary to resolve the matter.

Conclusion

We have shown that in the solvent-free oxidation of benzyl alcohol using supported Au–Pd/ TiO_2 nanoparticulate catalysts, a disproportionation reaction is the source of the major by-product, toluene (together with an equimolar amount of benzaldehyde), and oxidation by O_2 is the other source of benzaldehyde. We have demonstrated a reliable method of quantitatively separating the disproportionation reaction from the oxidation reaction in systems where both the reactions are active. Using this method, we have found that Au sites do not catalyse the disproportionation reaction, and Au sites are much less active for oxidation than Pd sites. By adding Pd to Au, we can increase the overall activity by a factor of 50, but at the expense of switching on the disproportionation reaction and thereby toluene formation. We have overcome this problem by changing the support from TiO_2 to either MgO or ZnO which give catalysts that are active only for oxidation. By comparing the oxidation reaction alone for all five catalyst systems studied, we have determined that they all have very similar activity. The higher overall activity found in the cases of activated-C-, Nb_2O_5 -

and TiO_2 -supported catalysts is due to the additional disproportionation reaction that occurs alongside the oxidation reaction. We conclude that the MgO- and ZnO-supported catalysts are superior to TiO_2 -, Nb_2O_5 - and activated-C-supported catalysts because they catalyse exclusively the oxidation reaction, yielding more than 99% selectivity to benzaldehyde. Further, a direct correlation has been observed between the structural interaction of Au–Pd nanoparticles with the support to the acidity/basicity of the metal oxide used to prepare the catalyst. We believe that the switching off of the disproportionation reaction for the MgO- and ZnO-supported catalysts takes place because they do not promote the formation of the required adsorbed species.

Experimental Section

Catalyst preparation: All the experiments were carried out using Au–Pd nanoparticles supported on various metal oxides as catalysts. These materials were prepared by a sol-immobilisation method.^[24] For the preparation of (Au–Pd)/ TiO_2 materials, aqueous solutions of PdCl_2 (Sigma Aldrich) and $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Sigma Aldrich) of the desired concentrations were prepared. Polyvinylalcohol (PVA) (1 wt% aqueous solution, Aldrich, MW = 10000, 80% hydrolysed) and an aqueous solution of NaBH_4 (0.1 M) were also prepared. To a mixed aqueous PdCl_2 and HAuCl_4 solution of the desired concentration, the required amount of a PVA solution (1 wt%) was added ($\text{PVA}/(\text{Au}+\text{Pd})$ (wt/wt) = 1.2); a freshly prepared solution of NaBH_4 (0.1 M, $\text{NaBH}_4/(\text{Au}+\text{Pd})$ (mol/mol) = 5) was then added to form a dark brown sol. After 30 min of sol generation, the colloid was immobilised by adding the support (TiO_2 : Degussa P25, Nb_2O_5 : Sigma Aldrich, activated C: Darco G-60 Sigma Aldrich, MgO: BDH, ZnO: Sigma Aldrich). For the catalysts with TiO_2 , Activated C and Nb_2O_5 as the supports 1 drop of conc. H_2SO_4 was added under vigorous stirring. The amount of support material required was calculated so as to have a total final metal loading of 1% wt. The metal ratio for the 1 wt% supported Au+Pd bimetallic catalyst was 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.

Benzyl alcohol oxidation: Benzyl alcohol oxidation was carried out in a 50 mL glass stirred reactor. In a typical reaction, the requisite amount of catalyst and substrate were charged into the reactor which was then purged with gas (He or O_2 as the case may be) three times before closing and the pressure was maintained at 1 bar (relative pressure). The reactor with the reaction mixture was kept in a heating block, which was preheated to the reaction temperature. The reaction mixture was stirred at 1000 rpm using a magnetic bar inside the reactor. After a specific time, the stirring was stopped and the reactor was rapidly cooled in an ice bath. After cooling for 10 min, the reactor was opened slowly and the contents were centrifuged. An aliquot of the clear supernatant reaction mixture (0.5 mL) was diluted with mesitylene (0.5 mL, external standard for GC analysis). Separate reactions were carried out for each particular point in the kinetic plot. The kinetic plot for one reaction was obtained by five different reactions that were stopped at different time intervals. For the analysis of the products, GC-MS (Waters, GCT Premier) and GC (a Varian star 3800 cx with a 30 m CP-Wax 52 CB column) were employed. The products were identified by comparison with known standards. For the quantification of the amounts of reactants consumed and products generated, an external calibration method was used. It was established that no reaction occurred in the absence of the Au–Pd catalyst or in the presence of the catalyst support alone.

Catalyst characterisation: Samples for examination by transmission electron microscopy (TEM) were prepared by dispersing the catalyst powder in high purity ethanol, then allowing a drop of the suspension to evaporate on a holey carbon film supported by a 300 mesh copper TEM grid. Samples were subjected to bright field diffraction contrast imaging in

order to determine particle-size distributions. The instrument used for this analysis was a JEOL 2000FX TEM operating at 200 kV. STEM high angle annular dark field (HAADF) images of the bimetallic particles were obtained using an aberration corrected JEOL 2200FS TEM operating at 200 kV.

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