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Solvent-free aerobic oxidation of alcohols using supported gold palladium nanoalloys prepared by a modified impregnation method

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Abstract

The synthesis of stable bimetallic nanoalloys with controlled size, morphology and composition is of great practical importance as they exhibit remarkable enhancement in functional properties when compared to their monometallic analogues, which can be exploited in various fields including catalysis. Recently, we have reported a simple excess anion modification of the impregnation method to prepare supported gold-palladium catalysts which gives very good control over the particle sizes and the composition without using any stabilizer ligands in the preparation. Here, we report the results from a comparative study of using this modified impregnation catalyst for the solvent-free aerobic oxidation of alcohols in two different reactors: glass stirred reactor and micro packed bed reactor under batch and continuous mode respectively. These modified impregnation catalysts are exceptionally active and more importantly, when tested in a micro packed bed reactor under flow conditions, are observed to be stable for several days without any sign of deactivation in contrast to the same catalyst prepared by the sol immobilization method in the presence of stabilizer ligands which showed a 3-5% decrease in conversion during 10-12 h.

Key words: gold catalysis, selective oxidation, catalyst deactivation

Introduction

The exceptional catalytic activity of gold nanoparticles has been reported in the literature for more than a quarter of a century.^{1,2} Since the crucial pre-requisite of these gold nanoparticles, to be catalytically active, is their size, numerous attempts have been made to prepare these nanoparticles as small as possible and with a very narrow particle size distribution.³⁻⁵ It is important to note here that the catalytic activity of gold nanoparticles, having a particle size above 10 nm, decreases dramatically.^{6,7} It has been reported that by combining gold with palladium at the nanoscale, the catalytic activity of these particles could be increased by several fold for the selective aerobic oxidation of alcohols.^{8,9} The catalytic activity for these bimetallic nanoparticles follows a similar trend to supported monometallic gold particles *i.e.*, catalytic activity increases with decreasing particle size. Due to this similarity, many methods of preparing supported monometallic gold nanoparticles have been directly translated to prepare supported bimetallic nanoparticles.^{4,10,11} However, the presence of a second metal can impose significant complications in terms of the particle size distribution, the mode of the arrangement of these two metals and the compositional variation from particle to particle.¹² These added complications pose significant challenges to the catalysis chemist to design methods to control these parameters. In an attempt to overcome these complications many synthetic methods have been developed over the years which include (a) wet impregnation,⁹ (b) incipient wetness,¹³ (c) deposition precipitation,⁴ (d) sol immobilization or colloidal deposition^{14,15} and (e) physical grinding of acetate salts.¹⁶ All of these methods have significant advantages as well as disadvantages; for example the conventional wet impregnation method (CI_m), for preparing supported gold-palladium nanoparticles, is a very simple method and has widely been practised. However, the resultant catalysts have nanoparticles ranging from sub-nm clusters up to nanoparticles 100 nm in diameter and there is no effective control over the particle size. To overcome this disadvantage, very small gold-

palladium nanoparticles were prepared in solution as sols using stabilizers ligands, for example polyvinyl alcohol (PVA) or polyvinyl pyridine (PVP), which exhibit very small particle sizes with a narrow distribution. These preformed nanoparticles are subsequently immobilized onto a solid support, for example a metal oxide; this method is called colloidal deposition or sol immobilization (SIm). Such catalysts have an improved catalytic activity for solvent-free aerobic oxidation of alcohols,^{10,17} but pose a different set of problems: the stabilizer ligands often block the active sites of such catalysts and these have to be removed either by high temperature calcination or by solvothermal treatments.¹⁸⁻²⁰ Another major problem with this method is the size dependent compositional variation; all the smaller particles are gold rich whereas the larger nanoparticles are palladium rich.^{3,12} Prüße and co-workers have previously reported the beneficial effect of using hydrochloric acid to dissolve tetrachloroauric acid when using the incipient wetness technique for the oxidation of glucose.²¹ They used a reduction step rather than calcination to activate the catalysts and reported that the hydrochloric acid precursor solution led to a final catalyst with a smaller average particle size when compared to the aqueous precursor. Recently, we reported an “excess-anion” modification of the CIm method to prepare 0.5wt%Au-0.5wt.%Pd supported on TiO₂ nanoparticles with precise control over the size, composition and nanostructure.²² The bimetallic catalysts, prepared by this modified impregnation (MIm) method, outperformed the identical catalysts prepared by CIm and SIm methods for the direct synthesis of hydrogen peroxide from a dilute mixture of hydrogen and oxygen.²²

Aerobic oxidation of benzyl alcohol has long been used as a model reaction for testing oxidation catalysts.^{23,24} Solvent-free oxidation of benzyl alcohol yields several products including toluene, benzoic acid, benzyl benzoate and dibenzyl ether, besides the desired benzaldehyde. Some of these products could be eliminated by careful design of the catalysts after understanding the origins of them.^{25,26} Conventionally, these reactions are performed

either in a glass stirred reactor or in an autoclave reactor in batch mode. Carrying out the reaction in a batch mode is not suitable for studying the long-term stability of the catalyst; continuous reaction is favoured for this. For multiphase reactions, involving a solid catalyst, liquid alcohol and gaseous oxidant, packed-bed flow reactor systems have the advantages of simplifying the process by eliminating separation of liquid products from the solid catalyst. For these three phase reactions, where mass transfer can be a limiting factor, micro reactors offer improved reaction rates and performance when compared to conventional macro reactors. Additionally, the small channels of the micro reactor offer efficient gas-liquid mixing along with sufficient gas-liquid-solid contact resulting in improved mass transfer in the packed bed of the catalyst.

In the present work we have studied the supported 0.5mol%Au-0.5mol%Pd nanoparticles catalysts in a batch reactor for the solvent-free aerobic oxidation of benzyl alcohol; the catalysts were prepared by the MIm method, and these were contrasted with catalysts prepared by CIm and SIm, that have identical Au:Pd ratios and metal content. The best catalyst was then tested for the oxidation of a range of alcohols. The long-term stability of equimolar 1%AuPd/TiO₂, prepared by SIm and MIm, was studied using micro-packed bed reactor (MPBR) for the oxidation of benzyl alcohol.

Results and Discussion

Solvent free aerobic oxidation of alcohols in glass stirred reactor (GSR)

1%AuPd/TiO₂ catalyst, having equimolar amounts of gold and palladium, was prepared by the MIm method using “excess-anion” methodology.^{21,22} For comparison, 1%AuPd/TiO₂, with identical metal content, was prepared by both CIm and SIm methods whose synthesis procedures and characterisation have been reported in detail elsewhere.^{9,25} The catalytic activities of these catalysts were tested for the solvent-free aerobic oxidation of benzyl

alcohol in a glass stirred reactor (GSR) at 120 °C and the results are presented in Table 1. From the conversion data it is clear that there are substantial differences in the catalytic activities of the catalysts prepared by three different methodologies which follow the order: MIm > SIm >> CIm. After 2 h reaction, CIm, SIm and MIm catalysts resulted in conversion of 14 %, 65 % and 88 % respectively. This clearly demonstrates the superiority of the current modified impregnation methodology over the other methodologies, especially the SIm method which has been reported to provide catalysts which are exceptionally active for the oxidation of alcohols.²⁷ To test the applicability of this current MIm methodology for supports other than TiO₂, we then investigated the use of MgO as the support for gold palladium nanoparticles. We specifically made this choice because MgO-supported AuPd catalysts have previously been reported to be effective in switching off toluene formation in the solvent-free aerobic oxidation of benzyl alcohol to yield benzaldehyde with approximately 99% molar selectivity.²⁵ The results from the oxidation of benzyl alcohol using 1%AuPd/MgO catalysts prepared by both the SIm and MIm methods are also presented in Table 1. Both catalysts show the equivalent selectivity towards the formation of benzaldehyde (98-99%) but the conversion for the MIm catalyst was found to be 33 % whereas the SIm catalyst resulted in 26% conversion. This set of results show that this MIm methodology delivers superior AuPd catalysts not only with TiO₂ as the support, but also with MgO. In our initial experiments, we have used only benzyl alcohol as the substrate for the oxidation reaction and our next objective was to test the tolerance of this catalyst to other substrates. To this end we evaluated the catalysts for the oxidation of crotyl alcohol (an aliphatic, primary allylic alcohol). These results are also presented in Table 1; again, the supported AuPd catalysts prepared by MIm methodology exhibited superior catalytic activity to those materials prepared by the SIm method.

Effect of HCl concentration on MIm catalysts

It is considered that Cl^- concentration plays a crucial role in keeping the metal ions separated during the impregnation stage, as discussed in our earlier study.²² Thus the effect of HCl concentration on the catalyst performance was studied. 1%AuPd/TiO₂ catalysts prepared by MIm with HCl concentration of 0, 0.58, 1 and 2 M respectively were prepared and evaluated for the oxidation of benzyl alcohol to benzaldehyde at 120 °C in a GSR. The results are given in Figure 1. It can be observed that in general the conversion of benzyl alcohol increases with HCl concentration from 76% at 0 M HCl (CIm) to 86% at 2 M HCl. With increasing HCl addition during the preparation, the selectivity to benzaldehyde decreases from 85% with zero HCl addition to 75% with HCl addition to give a final concentration of 0.58 M in the preparation. A further increase in the HCl concentration from 0.58 M to 2 M improves the selectivity from 75% to 84%. It is clear from these data that increasing the concentration of HCl leads to both an increase in the conversion of the benzyl alcohol and the selectivity of the desired product, benzaldehyde. However, we have previously reported that catalysts prepared with concentrations of greater than 0.58 M HCl are not stable under reaction conditions for the direct synthesis of hydrogen peroxide.²² The presence of chloride ions, used in MIm methodology, plays a crucial role in controlling the size and composition of supported AuPd nanoalloys.²² Supported AuPd nanoalloys prepared by CIm and SIm methodologies exhibit a complex size-dependent compositional variation.³ For catalysts prepared by the CIm methodology, all the larger particles are either exclusively gold or gold-rich, whereas all the smaller particles are palladium-rich.^{28,29} Catalysts prepared by the SIm methodology display a reverse trend, i.e., the smaller particles are Au-rich and the larger particles are Pd-rich. In the new MIm methodology, the presence of excess chloride ions eliminates the larger “gold-rich” particles and increases the Au concentration in the bimetallic particles.²² The concentration of Au in the bimetallic particles increases with the increase in

the chloride ion concentration. In addition to this, there was no size-dependent compositional variation observed for the catalysts prepared by this MIm methodology i.e., bimetallic particles of all sizes showed almost the same concentration of Au and Pd.¹² The superior catalytic activity for the materials prepared by this MIm methodology, observed in this work, is due to this precise control over the composition of Au and Pd in the nanoalloy particle.

Effect of thermal treatment conditions on MIm catalysts

The effect of thermal treatment of the material during the catalyst preparation was studied by varying the temperature and the gas environment of this step. A 1%AuPd/TiO₂ catalyst prepared by the MIm method was reduced at temperatures of 250, 300, 400 and 500 °C in flowing H₂/Ar. The aerobic oxidation of benzyl alcohol in the GSR was carried out to examine the performance of the reduced catalysts. The results, given in Table 2, show that the best performance is from the catalyst which is treated at 400 °C in H₂/Ar flow, achieving a conversion of 88% with selectivity 77% to benzaldehyde and 21% to toluene. The enhancement in activity as the reduction temperature increases could in part be due to both a decrease in the level of chloride on the surface coupled with surface oxidation of the Pd leading to the formation of PdO. Further increasing the thermal treatment temperature to 500 °C causes a marked decrease in conversion to ~26% and therefore we heat-treated catalysts at lower temperatures to maintain activity. With the thermal treatment at 400 °C in flowing air, the conversion of benzyl alcohol decreases to almost half of that obtained at a same temperature with H₂/Ar flow, to 45%, although the selectivity to benzaldehyde increases to 85%. For comparison, the catalyst prepared by the conventional impregnation technique was thermally treated at 400 °C in H₂/Ar flow. This catalyst gave a conversion of 76% (Table 2) demonstrating that the thermal treatment of the catalysts plays an important role in their activity and furthermore that reduction treatment should be considered as an alternative to oxidation treatments when preparing gold palladium bimetallic catalysts for oxidation

reactions. The high-temperature thermal treatment plays an important role in deciding the final nanostructure of the bimetallic nanoalloys. High-temperature calcination leads to the formation of a structure with a Au-core Pd-shell, whereas high temperature reduction results in a homogeneous random alloy structure.^{28,29} This is reflected in the Pd/Au surface ratio determined by XPS measurements (Table 3 and Table 4). Core-Shell nanostructures always give higher Pd/Au ratio compared to homogeneous random alloy structure (Table 3 and Table 4). As the reduction temperature increases from 250 °C to 500 °C the surface Pd/Au ratio decreases from 1.5 to 0.9. The Pd²⁺: Pd⁰ ratio decreases with increase in reduction temperature. Based on our previous STEM and XPS results in the case of 0.5wt.%Au-0.5wt.%Pd/TiO₂ and our current XPS results, we confidently conclude that in the current catalytic system (0.5mol%Au-0.5mol%Pd/ TiO₂) the gas-phase reduced catalysts have a homogeneous random alloy structure and the calcined catalysts have a Au_{core}-Pd_{shell} nanostructure. This difference in nanostructures is one of the contributing factors for the observed difference in the catalytic activities of the materials that underwent different thermal treatments. For alcohol oxidation, the homogeneous random alloy structure is more active compared to the core-shell structure. It is important to note that the catalysts prepared by SIM methodology always have a homogeneous random alloy structure.

Catalytic stability of 1%AuPd/TiO₂ MIM catalysts

In the literature, there are reports describing catalysts which are extremely active but lack stability over longer reaction times.^{30,31} To test the long-term stability of the present catalyst, it was evaluated for the continuous aerobic oxidation of benzyl alcohol in a micro-packed bed reactor (MPBR) at 120 °C over 75 h. During the test, samples were taken at 1-2 h intervals and analysed during the daytime, while overnight only one sample was taken and the analysed data was recorded as an average over the night period. Since a syringe pump was used for the delivery of benzyl alcohol to the MPBR, the syringe (2.5 ml) needed to be

refilled every 12 hours which caused about a 5-minute interruption to the reaction. The details about MPBRs and experimental procedure for this reaction have been reported elsewhere^{32,33} and are also available in the experimental section of this paper. The conversion and selectivity of the reaction on the MIm catalyst against the reaction time are shown in Fig. 2b. It is observed that the MIm catalyst showed catalytic activity (*ca.* 80% conversion) which is very similar to that found for the reaction in a GSR at the same space time and exhibited very good stability over the whole time period, here the space times in MPBR and GSR.

For comparison, a SIm catalyst of the same wt% composition was tested under exactly the same reaction conditions in a MPBR and the results are presented in Figure 2a. The SIm catalyst showed a lower reactivity (*ca.* 55% conversion on average) by comparison to MIm catalyst at a same catalyst loading. Deactivation of the catalyst was observed as the conversion declined *ca.* 3-5% in 10-12 h. The catalyst appeared to be reactivated after refilling the syringe which caused an interruption to the reaction and a very short period of exposure of the catalyst in O₂ under the reaction temperature. The sensitivity of the SIm catalyst to reaction conditions was also observed in a study of the effect of pretreatment on the catalyst stability, where a set of experiments were designed to treat the catalyst in the reaction mixture at 80-120 °C or in O₂ at 120-140 °C before starting the reaction. Figure 3 shows the conversions of benzyl alcohol on the SIm and the MIm catalysts at different pretreatment stages. It can be seen that for the SIm catalyst, pretreating in the reaction mixture from 80 to 120 °C produces catalysts with poor stability. The catalyst stability is much improved when the catalyst is pretreated in O₂ at 120 °C. However, for the MIm catalyst, the stability of the catalyst is almost unaffected by the pre-treatments. This study of the catalyst stability in micro-packed bed reactors (MPBRs) clearly showed the long term stability of the MIm catalyst and its much improved catalytic activity. The enhanced stability of the MIm catalyst we observe in these studies is considered to be due to the combination of

gold-rich bimetallic particles with almost no size-dependent compositional variation coupled with the high-temperature thermal treatment.

X-ray Photoelectron Spectroscopy (XPS) Analysis

XPS analysis of the MIm samples subjected to the different treatment regimes, revealed similar Au(4f) and Pd(3d) binding energies throughout the series of treatments, however, appreciable differences in the Pd²⁺/Pd⁰ and Pd/Au ratios were noted (Table 3).

Considering first the Au(4f) signals, binding energies *ca.* 82.5 eV were observed which are much lower than those expected for bulk-like metallic gold (*ca.* 84.0 eV), and even those of small particles where a shift of *ca.* 0.5 eV to lower binding energy is noted as a consequence of the lower surface atom coordination.³⁴ Clearly, the values reported here are a further 1 eV lower and are consistent with those noted previously for samples treated in H₂.^{18,35} This effect has been attributed to an increased initial-state contribution to the photoemission process, which has been calculated to manifest as a lowering of the expected energy by 1.1 - 1.5 eV.³⁶ Such changes have also been ascribed to charge transfer from Pd to Au, increasing the Au *s*-state occupancy during alloy formation or electron transfer from support to nanoparticle.¹⁸

Pd(3d) energies, determined through curve-fitting, are consistent with both metallic Pd (334.1 eV) and Pd²⁺ (336.1 eV) states, with the latter ascribed to PdO,³⁷ with increasing temperatures under the reducing H₂ atmosphere, a steady rise of the metallic Pd signal is observed (Table 3). The presence of Pd²⁺ is unsurprising avoided since samples are air handled before insertion in to the spectrometer.

It is interesting to see how the Pd/Au ratio is affected by the different thermal treatments. The theoretical Pd:Au ratio in the Au-Pd catalysts is 1:1 by weight; equivalent to a Pd:Au atom

ratio of 1.9:1,⁴ with the ratio for the best catalyst in the present study not too dissimilar from this theoretical value. Higher temperature treatment (500 °C) decreases this ratio to 0.9:1, possibly indicating Au enrichment of the surface of an Au-Pd alloy. It may be this which is responsible for the higher selectivity towards benzaldehyde (albeit at much lower conversion), with the Au minimising the sites for disproportionation to toluene.³ By comparison, the CIm sample treated at 400 °C under H₂/Ar, revealed a Pd/Au ratio of 7.7. Such a large increase over that expected for homogeneous alloys, or equally dispersed monometallic Au and Pd particles, may reflect particle size changes, and would be consistent with the weak signal, and therefore apparent low concentration, of Au.

Interestingly for the MIm H₂/Ar treated samples, Cl is detected for samples treated below 400 °C, whereas for 400 °C and above, no Cl is observed within the detection limits of the XPS spectrometer employed in this study. Whilst it is known that halides can have a promoting effect on the formation of Pd-O bonds,³⁸ and is demonstrated herein by the equivalent CIm sample which has a high level of Pd²⁺, with larger Cl concentration (comparable to the MIm sample treated at 250 °C) it should not detract from the observation that with increasing temperature and reductive atmosphere, the relative amount of metallic Pd increases together with the removal of Cl in the formation of active and selective catalysts.

Conclusions

A modified impregnation methodology for preparing supported gold-palladium nanoalloy catalysts in the presence of an excess amount of chloride ligands in the impregnation medium has been developed. Catalysts prepared by this method are found to be extremely active for the aerobic oxidation of alcohols and superior to similar composition catalysts prepared by other methodologies such as sol-immobilization and conventional impregnation. The catalysts prepared by this new methodology are found to be more active and stable for the

oxidation of alcohols to corresponding aldehyde than those made by conventional impregnation and sol-mobilisation methods. This provides both the academic research community and the industrial community, with a very convenient and reproducible methodology for preparing supported Au-Pd nanoalloy catalysts with high activity and stability without using any exotic ligands or stabilizers, while at the same time not compromising the catalytic activity.

Experimental Section

Catalyst preparation

Modified Impregnation (MIm) Method:

For the preparation of 1%AuPd supported catalyst, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Sigma Aldrich) and PdCl_2 (Sigma Aldrich) were used as a metals precursors. In a typical synthesis run, the requisite amount of aqueous gold (8.9ml/ml) and palladium solution (6mg/ml; HCl concentration: 0, 0.58, 1, 2 M) were charged into a clean 50 mL round-bottom flask fitted with a magnetic stirrer bar. The volume of the solution was adjusted using deionized water to a total volume of 16 mL. The flask was then immersed into an oil bath sitting on a magnetic stirrer hot plate. The solution was stirred vigorously at 1000 rpm and the temperature of the oil bath was raised from room temperature to 60 °C over a period of 10 min. At 60 °C, 1.98 g of the metal oxide support material [TiO_2 (Degussa Evonik P25) or MgO (BDH)] was added slowly over a period of 8-10 min with constant stirring. After the completion of addition of the support material, the slurry was stirred at 60 °C for an additional 15 min. Following this, the temperature of the oil bath was raised to 95 °C, and the slurry was stirred at that temperature overnight until all the water evaporated leaving a dry solid. Subsequently the solid powder was transferred into a mortar and pestle and was ground thoroughly to form a uniform mixture. This was stored and designated as a “dried-only” sample. For calcination/reduction, a portion of 400 mg of the uncalcined sample was transferred and spread out over a glass

calcination boat (30 cm in length). This boat was then placed inside a calcination furnace fitted with an inlet and outlet valve. Heating rate of 10 °C/min under a steady flow of gas (5% H_2 /Ar or Air) was used for calcination or reduction respectively in range of different temperatures (250 °C - 500 °C). After the furnace was cooled, the sample was used and denoted MIm catalyst.

Conventional Impregnation (CIm) Method

Detailed synthesis procedure for the CIm method is typically carried out as follows. To prepare 1%AuPd/TiO₂ the requisite amount of the metal precursors ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ for Au and PdCl_2 for Pd) were wet impregnated on to the solid support [TiO₂ (Degussa P25)]. The requisite amount of solid PdCl_2 was added to a predetermined volume of an aqueous solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and stirred vigorously at 80 °C until the palladium salt completely dissolved. The metal concentrations were maintained in such a way that the Pd/Au molar ratio equals 1 and the total weight percentage of the metal was kept as 1%. After that, the requisite amount of the support was added to this solution under vigorous stirring conditions. The solution was agitated at 80 °C in this way until it formed a paste, which was then dried at 120 °C for 16 h and then calcined in static air, typically at 400 °C for 4 h. This catalyst is labelled as CIm catalysts.

Sol Immobilization (SIm) Method:

Catalysts were prepared using a well-established sol immobilization methodology whose procedure is reported elsewhere in detail.^{3,18} In a typical catalyst synthesis (1%AuPd/TiO₂) 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. The metal concentrations were maintained in such a

way that the Pd/Au molar ratio equals 1 and the total weight percentage of the metal was kept as 1%. Polyvinyl alcohol (PVA) (1 wt % aqueous solution, Aldrich, MW = 10000, 80% hydrolyzed) and an aqueous solution of NaBH₄ (0.1 M) were also prepared. To an aqueous mixture of PdCl₂ and HAuCl₄ solution of the desired concentration, the required amount of a PVA solution (1 wt %) was added (PVA/(Au+Pd) (w/w) = 1.3). 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 support material (TiO₂, Degussa P25; MgO, BDH). For the catalysts prepared with TiO₂ as the support, 1 drop of concentrated H₂SO₄ 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 Au+Pd bimetallic catalyst was 1:1 by weight. After 2 h, the slurry was filtered, and the catalyst was washed thoroughly with 2 L of distilled water (until the mother liquor was neutral) and then dried at 120 °C overnight under static air.

Solvent-free alcohol oxidation in a batch reactor

Alcohols oxidation was carried out in a Radleys carousel reactor using a 50 mL glass stirred reactor. In a typical reaction, the requisite amounts of catalyst and substrate were charged into the reactor at room temperature which was then purged with the required gas (O₂) three times before the reactor was sealed using a Teflon screw threaded cap. The reactor was always connected to the gas-line to ensure the consumed gas was replenished. The pressure was monitored using the pressure gauge fitted in the inlet line.

The reactor with the reaction mixture was loaded into a preheated heating block, which was maintained at the reaction temperature. The reaction started by commencing 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 slowly and the contents were centrifuged. An aliquot of the clear supernatant reaction mixture (0.5 mL) was then diluted with mesitylene (0.5 mL) for GC analysis. It was also verified that no reaction occurred in the absence of the catalyst or in the presence of the catalyst support alone. This experimental method is identical to our standard reaction protocols for solvent-free benzyl alcohol oxidation reported elsewhere.^{22,25} The turnover frequency (TOF) was calculated from the moles of substrate consumed and the total number of moles of metal present in the catalyst. Here, we assume that all kinds of metal sites are catalytically active.

Solvent-free aerobic oxidation of benzyl alcohol in micro packed bed reactor (MPBR)

The overall size of the silicon/glass microreactor chip used was 23 mm × 23 mm with a reaction channel dimension of 0.6 mm (W) × 0.3 mm (H) × 190 mm (L). A pillar structure (small rectangular posts of 60 μm (W) × 1 mm (L)) was arranged at 40 μm intervals near the outlet of the reaction channel to retain the catalyst. A schematic representation and the detailed procedure of operating MPBR are presented elsewhere.^{32,33} The prepared catalyst powder was pelletized and then crushed to obtain the desired particle size fraction by sieving. The catalyst was introduced into the reaction channel through the gas inlet with the help of a vacuum pulled at the outlet of the reaction channel. The packed microreactor was then assembled with a heating and temperature control unit. During the reaction, benzyl alcohol was delivered into the reactor by a syringe pump. Gases were regulated by mass flow controllers (Brooks 5850TR) and directed to the gas inlet of the reactor. The gas flow rate reported here is in mL/min at Standard Temperature and Pressure (STP, 273K and 1.01325 bar). The effluent from the reactor passed into a small glass vial (2 ml) which was located in a cold trap (ice-water bath), where gas and liquid were separated.

Experiments were normally started by treating the catalyst with O₂ at 393K for 60 min. The reaction was started by introducing benzyl alcohol at a specified flow rate. After 30 min, liquid product was collected and analyzed at pre-determined time intervals during day time. Over the night period, only one sample was taken and the analysed data was recorded as an average over the night period. The syringe (2.5 ml) needed to be refilled every 12 hours which caused about a 5 min interruption to the reaction.

The space times (ST) in the MPBR and GSR are defined as:

$$\text{In MPBR, } ST = \frac{\text{mass of catalyst (g}_{\text{cat}})}{\text{alcohol mass flow - rate (g}_{\text{alc}}/\text{s})} \quad \text{g}_{\text{cat}}\text{s g}_{\text{alc}}^{-1}$$

$$\text{In GSR, } ST = \frac{\text{mass of catalyst (g}_{\text{cat}})}{\text{mass of alcohol (g}_{\text{alc}})} \times \text{reaction time (s)} \quad \text{g}_{\text{cat}}\text{s g}_{\text{alc}}^{-1}$$

Product Analysis

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, using mesitylene as the external standard, was used.

X-ray Photoelectron Spectroscopy (XPS)

A Kratos Axis Ultra DLD system was used to collect XPS spectra using monochromatic Al K α X-ray source operating at 120 W. Data was collected in the Hybrid mode of operation, using a combination of magnetic and electrostatic lenses, over an area approximately 700 \times 300 μm^2 at pass energies of 40 and 160 eV for high resolution and survey spectra respectively. Magnetically confined charge compensation was used to minimize sample charging and the resulting spectra were calibrated to the C(1s) line at 284.7 eV.

Transmission Electron Microscopic (TEM)

Analysis was performed in a JEOL 2100 TEM instrument. The powdered samples were dispersed in deionised water before being added to holey carbon film on copper grids. EDX analysis was performed using Oxford Instruments SDD detector XmaxN 80T and analysed using Aztec software. Particle size distributions were determined using ImageJ software and 150 particles were counted for this.

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Notes:

The authors declare no competing financial interests.

Author contributions:

MM and EN prepared the catalysts and performed catalytic experiments under the supervision of MS. EC performed experiments in MPBR under the supervision of AG. DM performed the XPS characterization of all the materials. EN, PJM and TD performed other characterization of catalysts. DWK and DB helped in the discussion and interpretation of the data. GJH directed this research program. All authors commented and contributed in writing this manuscript.

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Table 1: Aerobic oxidation of alcohols in a glass stirred reactor using 1%AuPd supported on TiO₂ and MgO catalysts prepared by different methods ^a

Substrate	Catalyst	Synthesis method	Conv. (%)	Selectivity* (%)	TOF [†] (h ⁻¹)
Benzyl Alcohol	1%(AuPd)/TiO ₂	CIm	14	80	940
		SIm	65	80	4600
		MIm	88	77	6100
	1%(AuPd)/MgO	SIm	26	99	1900
		MIm	33	98	2300
Crotyl alcohol	1%(AuPd)/TiO ₂	SIm	8	42	390 [▲]
		MIm	18	45	920 [▲]
	1%(AuPd)/MgO	SIm	7	41	760
		MIm	12	47	1200

^a alcohol: 2 g, catalyst : 0.02g, temperature : 120 °C, pO₂: 1 bar, stirring speed:1000 rpm, time = 2h. CIm catalysts: calcined at 400 °C/4h

SIm catalysts: dried at 120 °C/16h

MIm catalysts: Prepared in a 0.58M HCl and reduced at 400 °C/4h.

* Selectivity to the corresponding aldehyde.

[†] TOF after 2h of reaction.

[▲] TOF after 4h of reaction

Table 2: Aerobic oxidation of benzyl alcohol in a glass stirred reactor using 1%AuPd supported on TiO₂ with different catalyst high temperature treatment procedures ^a

Catalyst (Synthesis method)	Heat Treatment Temperature ° C	Heat Treatment Atmosphere	Conv. (%)	Selectivity (%)*	
				Aldehyde	Toluene
1% AuPd/TiO ₂ (MIm)	250	H ₂ /Ar	79.7	77	22
	300	H ₂ /Ar	78.5	80	19
	400	H ₂ /Ar	88	77	21
	500	H ₂ /Ar	25.7	92	6
	400	Air	45	85	11
1% AuPd/TiO ₂ (CIm).	400	H ₂ /Ar	76	85	11
	400	Air	14	80	18

^a substrate = 2g, catalyst = 0.02g, temperature = 120°C, pO₂= 1 bar, stirring speed = 1000

rpm, time = 2h. All the MIm catalysts were prepared in a 0.58M HCl solution.

* other products include benzyl benzoate and benzoic acid

Table 3: Quantified XPS results for 0.58M HCl MIm prepared samples. The Cl, Pd and Au atom % compositions are mean values for the surface region samples by XPS. The CIm H₂/Ar sample is included as a comparison.

Treatment	MIm					CIm				
	% Cl	% Pd ^a	% Au	Pd/Au ^b	Pd ²⁺ :Pd ⁰ ^c	% Cl	% Pd ^a	% Au	Pd/Au ^b	Pd ²⁺ :Pd ⁰ ^c
H ₂ /Ar 250 ° C	0.53	0.28	0.14	1.5	d	--	--	--	--	--
H ₂ /Ar 300 ° C	0.35	0.31	0.12	2.1	1.1:1	--	--	--	--	--
H ₂ /Ar 400 ° C	0	0.25	0.11	1.8	0.75:1	0.5 3	0.49	0.06	7.7	2.23:1
H ₂ /Ar 500 ° C	0	0.25	0.18	0.9	0.32:1	--	--	--	--	--
Air 400 ° C	0	0.24	0.09	2.2	1.43:1	--	--	--	--	--

^a Calculated from the apparent Pd(3d) intensity, which incorporates intensity from the Au(4d_{5/2}) component

^b Ratio corrected for the overlap of the Pd(3d) doublet and the Au(4d_{5/2}) component

^c Ratio of Pd species determined by curve-fitting analysis

^d Due to the weak Pd signal, the ratio cannot be ascertained, however the most intense spectral intensity is at a binding energy for Pd⁰.

Table 4: Comparison of fresh and spent catalysts (1%AuPd/TiO₂) prepared by CIm, SIm and MIm methodologies ^[a]

Synthesis Methodology	Nature of the catalyst	Particle Size ^[b]	Pd/Au Ratio ^[c]
CIm	Fresh	4.7	8.1
	Spent (GSR)	3.9	3.8
SIm	Fresh	2.5	1.1
	Spent (GSR)	2.5	3
	Spent (MPBR)	3.8	2.4
	*Spent (MPBR)	3.0	3.7
	**Spent (MPBR)	3.0	4.8
MIm	Fresh	4.2	1.8
	Spent (GSR)	4.0	1
	Spent (MPBR)	4.5	1.2
	***Spent (MPBR)	3.8	1.1

The MIm catalysts were prepared in a 0.58M HCl solution.

*oxidation in O₂ at 120 °C for 1h

**activation in reaction mixture from 80 to 120°C before reaction overnight in O₂

***activation in reaction mixture from 80 to 120°C before reaction

[a] Corresponding histograms are presented in supporting information.

[b] The particle sizes were measured using TEM.

[c] The Pd/Au ratios were measured by XPS

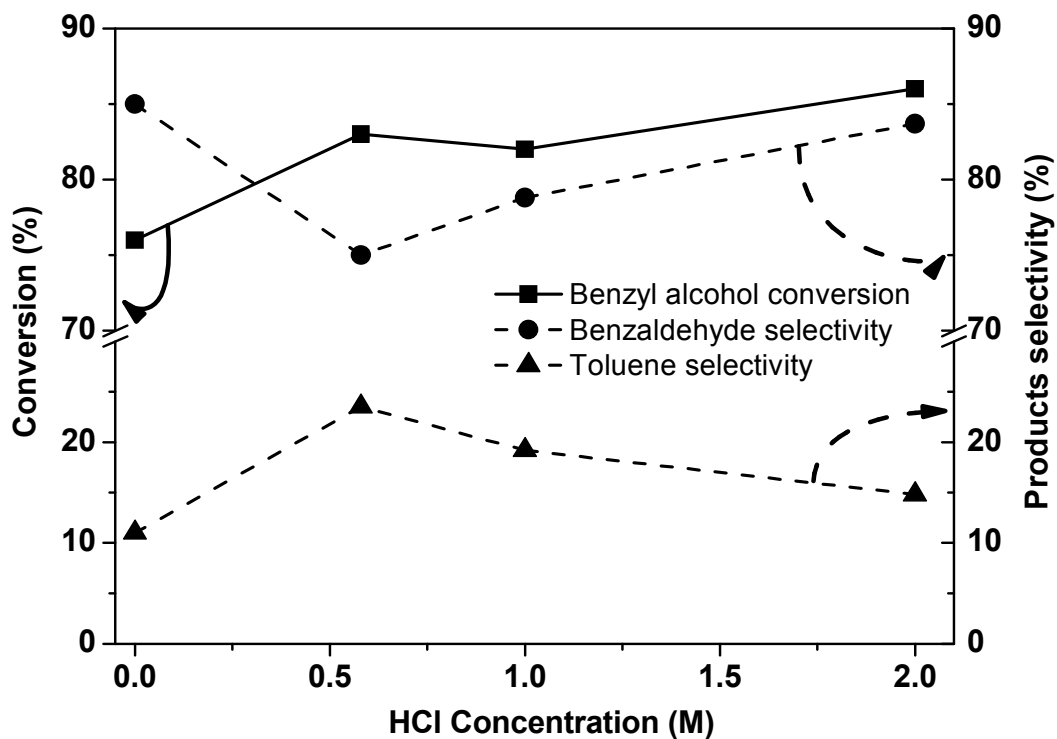


Figure 1: Effect of HCl amount, during catalyst preparation, on the catalytic performance of 1%AuPd/TiO₂ (MIm reduced at 400 °C) in a glass stirred reactor (GSR). Reaction conditions: benzyl alcohol = 2g, catalyst = 0.02g, temperature = 120 °C, pO₂= 1 bar, stirring speed = 1000 rpm, time = 2 h

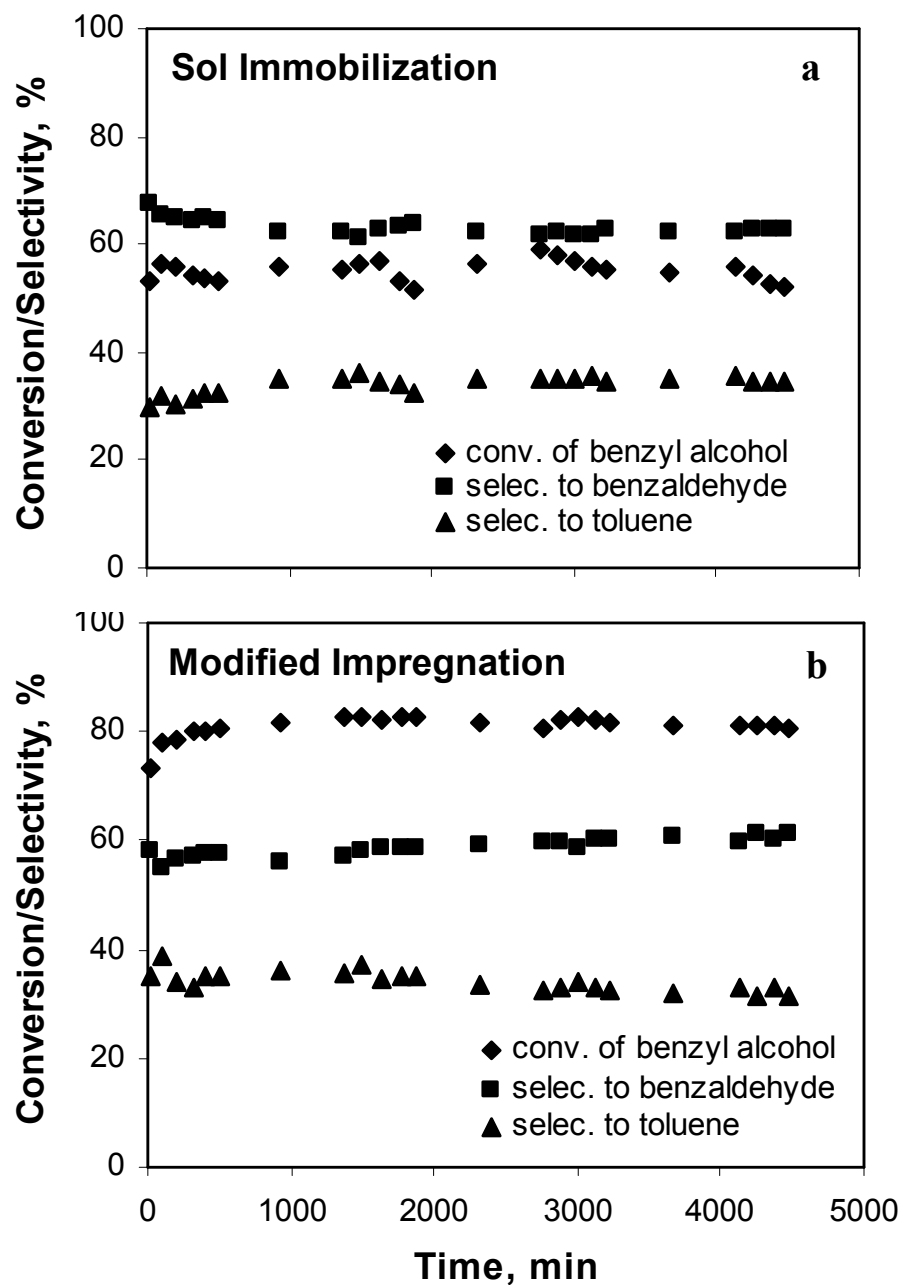


Figure 2 Oxidation of benzyl alcohol in micro-packed bed reactors (MPBRs) using 1%(AuPd)/TiO₂ catalysts prepared by a) the sol immobilization (SIm) and b) the modified impregnation (MIm, 0.58 M HCl, reduced at 400 °C) methods. Reaction conditions: catalyst weight 0.004 g, catalyst particle size 53-63 μm , benzyl alcohol flow 0.003 mL/min, O₂ flow 0.6 mL/min, 120°C

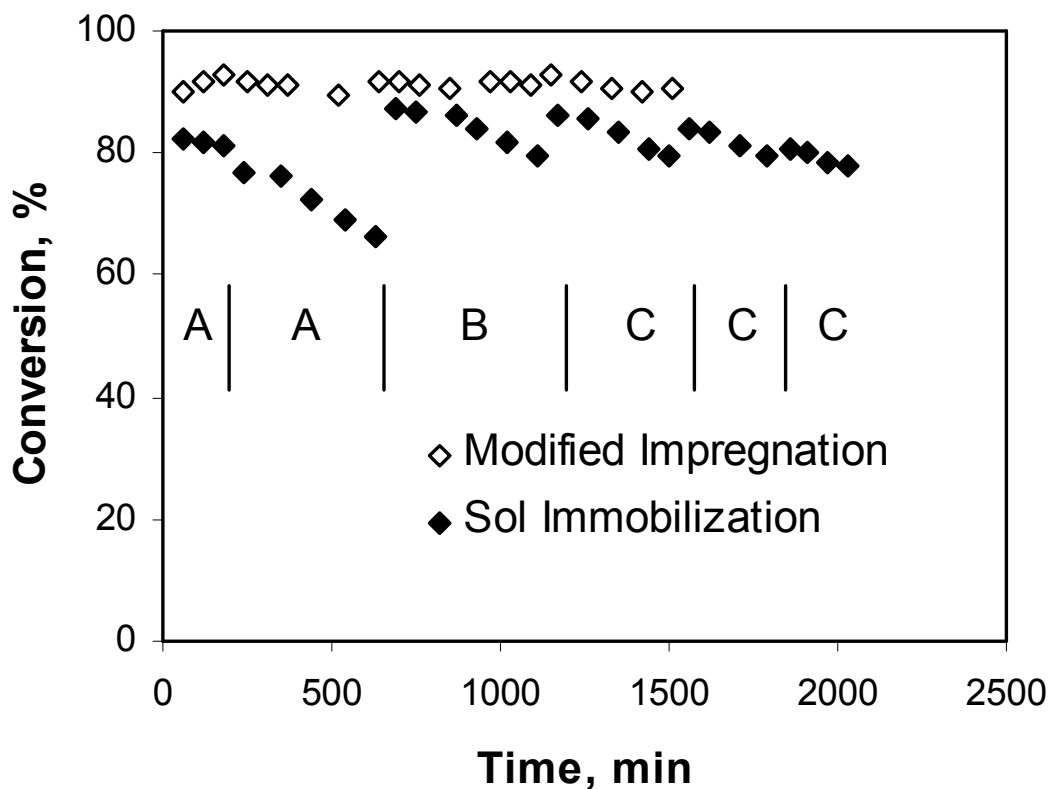


Figure 3 Effect of pre-treatment on the stability of the SIm and the MIm (0.58 M HCl, reduced at 400 °C) catalysts. Reaction conditions: SIm 0.0062 g, MIm 0.005 g; catalyst particle size 53-63 μm ; benzyl alcohol flow 0.003 mL/min, O₂ flow 0.6 mL/min; 120 °C. Pre-treatment: A—80 to 120°C in reaction mixture, B—140°C in O₂, C—120°C in O₂