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An insight into the superior performance of a heterogeneous Gold nanocatalyst supported by Single Walled Carbon Nanotubes compared to Titanium Dioxide and Amorphous Carbon for the green aerobic oxidation of aromatic alcohols.

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Abstract: Gold nanocomposites based on three supports (one novel and two industry-standard) were prepared using an in-situ reduction technique and characterised thoroughly to determine their physical properties. They were then tested for their suitability as heterogeneous catalysts in the green aerobic oxidation of one secondary and two primary aromatic alcohols of industrial importance. For all reactions, the use of single walled carbon nanotubes as supports (SWCNTs) was seen to result in superior reaction efficiency and specificity compared to gold nanoparticles supported on Titanium dioxide and amorphous carbon. In addition, the gold nanocatalysts used in this work can be reused over several reaction cycles with minimal degeneration in catalytic activity. There have been several discussions outlining the potential reasons why gold nanoparticle (Au NP) catalysts are so active, including particle shape, size and properties of the supports but there has been very little expansion on the optimisation of the catalytic activity. In this work, it is hypothesised that the position of the migrating functional group on the substrate, coupled with the properties of the support material and the particle size distributions (PSDs) of the active Au NP phase contribute to the high selectivity of these catalysts in these reaction types.
1. Introduction:

The use of nano gold particles (Au NPs) as an active phase in catalysis has taken off enormously since Haruta’s pioneering work in the area in 1989 [1]. Since then there has been a myriad of publications highlighting the high catalytic activity and selectivity in a large number of oxidation reactions of industrial importance, including the oxidation of glucose [2, 3], alcohols [4, 5] and polyols, most specifically glycerol [6, 7].

The oxidation of alcohols to their corresponding aldehydes or ketones is seen as one of the simplest and most useful transformations in organic chemistry and is at the core of an array of synthetic routes in industrial chemistry [8, 9]. Thus, the ability to catalyse these reactions under more ‘green’ conditions is highly desirable. Of concern is that most of the catalysts or processes that have been identified to date are relatively inactive for primary alkyl or secondary alcohols and those used generate heavy-metal waste. In addition, they are generally run using chlorinated solvents or acidified systems [10-12]. From a green point of view, using O₂ as an oxidant under atmospheric conditions in place of stoichiometric oxygen donors would be ideal, as H₂O would be the only by-product of the process. Nevertheless, using O₂ does raise safety concerns, particularly at high temperature and pressure, and so it is preferable to be able to use oxygen at atmospheric pressure.

Typically, catalyst systems used for these types of reactions require the use of solvents, so it is pertinent that the development of catalysts that can operate in a solventless system be explored in a drive to improve environmental friendliness. In addition, in order to endeavour to stay within the rigors of ‘green’ processes, it is necessary to either minimise or, whenever possible, eliminate the production of heavy metal or chlorinated waste generated during the reactions. Hence, a system in which the only by-product is water would potentially be a significant development of catalytic processes in industrial chemistry. Primary aromatic (benzylic) alcohols can be readily transformed to aldehydes that are relatively resistant to further oxidation, at least under mild conditions [13]. An example of this is the oxidation of benzyl alcohol (phenylmethanol), which is one of the most commonly reported test reactions and has been characterised extensively showing excellent selectivities and yields on almost all common catalysts [14].

However, there are very few probe reactions commonly used to compare different types of catalysts for the selective transformation of alcohol to aldehyde/ketone and/or carboxylic acid [15]. Also, more often than not, further oxidation of aldehydes to their corresponding acids is considered to be an undesirable side reaction and thus catalysts and processes are regularly optimised to avoid it. In a previous paper, we described the catalytic potential of Au/SWCNT for the liquid phase oxidation of 1-phenylethanol to acetophenone [16]. This work highlighted a preliminary use for SWCNT as a catalyst support in a 'green' reaction.

The object of this follow on work was to compare three supported gold nano composites as catalysts in the aerobic oxidation of three aromatic alcohols (one secondary and two primary) used as probe reactions and offer some insight into the role of the support materials in the selectivity of the catalysts themselves.
2. Experimental:

Titanium IV dioxide nanopowder and the SWCNT used in this work were sourced from Sigma-Aldrich. In the case of the SWCNT, prepared by the so-called Arc-Discharge Method [17], the reported composition is ~70% SWCNT (with single tube diameters between 1.2-1.5nm and bundles of lengths in the order of ~20µm), ~30% Amorphous Carbon and ≤ 1% Nickel/Yttrium [18]. The carbon black (P90) whose chemical composition is amorphous carbon was gifted by Degussa. Gold chloride (HAuCl₄) and sodium borohydride (NaBH₄) were also sourced from Sigma-Aldrich. Finally, doubly distilled water was obtained from a Millipore Elix 5 water purification system.

2.1. Catalyst Preparation and Characterisation:

For the preparation of the catalysts, the required amount of SWCNT, C or TiO₂ was suspended in double distilled water and stirred vigorously. The necessary volume of 0.02M HAuCl₄ solution required to obtain 5% AuNPs by weight on each support material was added dropwise with continuous stirring. The pH of the solution was maintained at ~8.5 by means of addition of 15% NaBH₄ [19]. The precipitated solution was aged under stirring for 2h. A solution of ice cold 0.02 M NaBH₄ was prepared and added as needed to complete the reduction of Au(III) to Au(0) and then the suspended solution was aged while maintaining the pH at 8.5 for a further 2h. The suspension was then filtered using a 0.45 µm nylon filter and washed with 3 times the suspension volume using doubly distilled H₂O and then the remaining solid mass was dried in an oven for a minimum of 4h at ~120 °C prior to characterisation.

Three supported gold nanocomposites, gold on titanium dioxide (Au/TiO₂), gold on single walled Au/SWCNT and gold on carbon black (Au/P90) were prepared and systematically characterised using Scanning Electron Microscopy/Scanning Transmission Electron Microscopy (SEM/STEM), Energy Dispersive X-Ray Analysis (EDX), X-Ray Diffraction Spectroscopy (XRD), Atomic Absorption Spectroscopy (AAS), (Nitrogen) N₂ adsorption, Ultra Violet-Visible (UV-Vis) absorption spectroscopy and Raman spectroscopy to probe the nanoparticle and support physical and chemical characteristics as well as the metal-support interactions. For all composites, the Au NPs were found to be crystalline with a well-defined and relatively narrow particle-size distribution, between 4-10nm. (Some representative images are shown in Figure 1). It is worth noting at this point that the SWCNT bundles were used as a support both before and after purification to remove the Ni/Y and there were no discernable differences in its performance with regard to catalytic activity hence the results are not reported here.
EDX analysis provided the initial confirmation of the presence of gold in the catalyst samples and XRD provided evidence of the formation of metallic Au NPs on the surface of the supports. AAS following acid digestion was used to determine the % gold by weight in each of the three catalysts. N₂ adsorption analysis showed an increase in surface area of the supports both before and after deposition of gold indicative of deposition of crystalline nanoparticles. UV-Vis absorption spectroscopy showed the existence of a gold plasmon resonance in the catalyst samples and using the spectrum of the absorption maximum allowed estimation of the gold particle sizes to be determined. Raman spectroscopy showed dampening in intensity of the characteristic bands in each sample due to the deposition of gold nanoparticles on the surface of the supports. In addition, evidence of changes in the characteristics of the single walled carbon nanotube support spectrum was seen; most specifically charge transfer which lends some insight into the behaviour of the Au/SWCNT catalyst and this is discussed in a previous paper [16]. Table 1 shows a list of some of the physical properties determined for each of the three nanocomposites. The EDX patterns, XRD patterns and the N₂ adsorption isotherms are provided in supplementary information.

UV-Vis characterisation (results provided in supplementary information) showed that the three composites exhibit the distinct Au nanoparticle plasmon absorption in the visible region, where as the Au/SWCNT system also has a well-defined plasmon absorption in the UV. The surface plasmon absorption in the Au nanoparticles arises from the combined oscillations of the free conduction band electrons that are generated by incident electromagnetic radiation [20] and, as the oscillations are localised on the surface, this plasmon absorption of Au nanoparticles is both strongly dependent on the nanoparticle size and sensitive to changes in the surrounding environment [21]. The narrower plasmon absorption band in both the Au/SWCNT and Au/P90 matrices compared to that seen from the Au/TiO₂ composite may be the result of slightly smaller diameters observed for the nanoparticles in the former two composites. Literature has already shown that smaller Au nanoparticles are more active for catalysis and this suggests that even the subtest difference in average Au particle size between the composites can have a large reaching effect on their activity [22]. Alternately, the changes in the plasmon bands may suggest an interaction at the particle/matrix interface in these composites which results in a change in the free electron density in the Au nanoparticles induced by charge transfer [23]. Either or a combination of these phenomena could affect catalytic activity of the Au nanoparticle composites.

Raman analysis (see supplementary information) of both the SWCNT support and the Au/SWCNT composite also point towards change in the nanotube characteristics as a result of the Au deposition. The G’ band shifts upfield in the composite sample which is indicative of charge transfer in the sample [24]. The RBMs have also changed their shape, shifted downfield and decreased in intensity. These significant changes can be attributed to debundling due to changes in the environment of the system or to charge transfer to the nanotubes filling previously unoccupied electronic states. The formation of Au nanoparticles onto the sidewalls of SWCNT bundles has been attributed to direct redox reduction between the nanotubes and the metal ions in solution [25]. In effect, this means that the nanotube/Au³⁺ systems can be categorised as redox pairs which would be expected to cause an enhancement in the conduction of the system which could account for the catalytic rate of the Au/SWCNT system being more efficient than that of the traditional TiO₂ and C supported systems (shown later). An example of redox pairs is the galvanic cell in which Zn and a Cu²⁺ solution, spontaneous oxidation of Zn to Zn²⁺ and reduction of Cu³⁺ to Cu occurs [26]. The work function and Fermi levels of SWCNT have been shown to be above the reduction potentials of AuCl⁴⁻ which rationalises the spontaneous electron/charge transfer from the nanotubes to the metal ions and their subsequent reduction [27-28].
2.2. Oxidation Reactions studied:

Three alcohols (one secondary and two primary), 1-phenylethanol, 2-phenylethanol and benzylalcohol were used as probe substrates for solventless aerobic oxidation reactions using of the three composite materials in turn to ascertain if they could be used as heterogeneous catalysts. Our initial work in this area published previously [16] highlights the use of a single walled carbon nanotube supported gold nanocomposite as a potential catalyst for oxidation reactions. The reactions concerned and their conditions are shown in Tables 2-4.

The % conversion and % selectivity of the reactions are calculated using Equations 1 and 2 respectively.

Conversion of the alcohol is defined based on the initial (C₀) and final (C₁) molar concentrations of the substrate:-

Equation 1: \% Conv = 100 \times \frac{([C₀] - [C₁])}{[C₀]}.

Selectivity to the aldehyde, carboxylic acid or ketone is defined as the ratio of the molar concentration of the aldehyde, carboxylic acid or ketone formed during the reaction (C₂) to the molar concentration of substrate (C₁) converted in the same time:-

Equation 2: \% Sel. = 100 \times \frac{[C₂]}{([C₀]-[C₁])}.

3: Results and Discussion:

3.1: Aerobic Oxidation of 1-phenylethanol

While all three nanocomposites catalyse the oxidation to the expected ketone, there are some distinct variations in their performances (shown in Table 1). The Au/TiO₂ catalyst is 100% selective to the formation of its corresponding ketone within ~ 8hr, while the Au/SWCNT catalyst is 100% selective to formation of the ketone within ~ 3hr. The Au/P90 catalyst promotes the production of a secondary product, determined by FT-IR and NMR spectroscopy to be ethylbenzene (~35%), alongside acetophenone (~65%), most likely due to either the active carbon support acting as a reductant or its capacity for trapping hydrogen during its synthesis [29]. Figure 2 (in supplementary data) shows the conversion profiles for the aforementioned reaction.

3.1.2: Discussion of Au/P90 results

Notably, under similar reaction conditions using Pd/CeO₂ and Pd/apatite catalysts, ethylbenzene was reported to be formed as a by-product [30], although no explanation was proposed for this occurrence. With this exception, no other products have been reported from the aerobic oxidation of 1-Phenylethanol other than the expected acetophenone. In the case of Au/P90 catalyst, it is clear that it played an active part in the reaction, as the % conversion to acetophenone was 65%. Conversely the production of ethylbenzene under these conditions could be possible with the presence of surface carbon acting as a reductant and producing CO and ethylbenzene alongside oxidation to the ketone.

Alternatively, surface H could remain behind on the catalyst after manufacture, although this is a less likely scenario. The only way envisaged for surface H to be present in the catalyst is if it were retained within the surface structure during the preparation of the catalyst which is made using the precursor salt HAuCl₄ and using a reducing agent NaBH₄. It would appear that, despite washing the
catalyst as per standard protocol [31], not all of the H\(^+\) ions are removed, but remain adhered to the catalyst surface during the drying process. In essence, the amorphous carbon support acts as a hydrogen trap.

This would mean that if the active sites on the catalyst are strongly basic when it is in suspension with the substrate and, it is possible that hydrogenation of 1-Phenylethanol could occur if the reactant itself was to behave as a hydrogen acceptor. Bearing this in mind, it is suspected that the O\(_2\) reduction mechanism would be quite complex, involving competing reaction routes. The most straightforward one in this case would be the stepwise partial oxidation via a phenyethoxy intermediate namely from O\(_2\) to O* and then hydrogenation to ethylbenzene by released H atoms adhered to the surface of the catalyst and, in parallel, the generic oxidation with loss of hydrogen to form acetophenone.

3.2: Recycled Catalyst Cycles:

In the interests of determining both the catalyst stability in the case of all three nanocomposites and to further investigate the nature of the results yielded using the Au/P90 catalyst, it was necessary to repeat the reactions using recycled catalyst aliquots for each of the three composites over at least three reaction cycles. Between cycles, the catalyst was collected after filtration, washed thoroughly using acetone which has been reported to promote catalyst regeneration [32] and deionised water, then finally dried at ~120ºC overnight prior to redeployment.

All three catalysts demonstrated good reusability over three reaction cycles and almost identical selectivities within the same timeframe with only marginal decrease in activity which would be expected over several cycles (not shown) [33].

Following on from the aforementioned dual product formation using the Au/P90 composite, the reaction was repeated using recycled Au/P90 catalyst material for an extended five full reaction cycles. The secondary reaction ceases when the catalyst is recycled which suggests that either the remaining Au/P90 catalyst has ceased to produce CO and has stabilised or that the hydrogen trapped in the support is either used up as the catalyst is turned over or removed during the washing process between cycles [29].

The production of ethylbenzene under these conditions could be possible with the presence of surface carbon acting as a reductant producing CO and ethylbenzene alongside oxidation to the ketone. As the reaction cycles ensued, the % conversion to acetophenone increased and the formation of ethylbenzene reduced and ceased, as would be expected if the active carbon support P90 acted as a reductant producing CO but once this CO production ceased, the Au/C remaining was now stable as a selective oxidation catalyst.

Alternatively, if there was excess H on the catalyst surface, the surface H would be removed as the reaction took place over a number of cycles. As the concurrent formation of ethylbenzene decreased and then ceased after the second reaction cycle this could be consistent with a release of trapped hydrogen atoms which in turn are consumed during the repeated reaction process or slowly removed during the washing of the composite material between reaction cycles [34]. There is also an increase in water production as the ethylbenzene production decreases consistent with a shift to Route 1 as the residual surface hydrogen in the composite is consumed. The production of water would be completely normal under these reaction conditions. The ethylbenzene production could possibly be attributed to free radical formation due to reactive oxygen species such as a hydroxyl radical being formed but detailed EPR spin trapping and oxygen monitoring techniques utilised for other oxidation
type reactions [35, 36, 40] would be required to attempt to determine and devise a detailed mechanistic pathway which is outside the scope of this work.

While all three composites show catalytic potential in this reaction type, the Au/SWCNT composite in this preliminary reaction showed the most promise in terms of reaction rate. In order to determine the true catalytic potential of each of the catalysts, their reactivities were analysed in a more challenging system [37].

The variation in time taken for the reactions to go to completion could be potentially attributed to the Au particle sizes which for the Au/TiO$_2$ catalyst are larger (10-20 nm) than those of both the Au/SWCNT and Au/P90 that are between (4-7 nm) and (7-9 nm) respectively. As is widely reported in the literature, oxidation over gold is very sensitive to particle size [38, 39, 41-42] so this could go some way to explaining the difference in time taken for the reactions to go to completion.

In addition, the Au nanoparticle size distribution on the SWCNT support was seen to be more homogeneous than that on the TiO$_2$ support. This in turn could be ascribed to the significantly lower surface area of the TiO$_2$ supported composite (~23 m$^2$ g$^{-1}$) in contrast to that of the SWCNT supported catalyst (265 m$^2$ g$^{-1}$). This in turn would be likely to increase the number of exposed active catalyst sites for the adsorption of O$_2$ which would subsequently be responsible for the increased reaction rate. The surface area of the Au/TiO$_2$ catalyst is over a factor of ten less than that of the Au/SWCNT catalyst, so this is possibly another contributory factor for the time taken for the reaction to go to completion to reduce from 8 h to 3 h.

3.3 Aerobic oxidation of 2-phenylethanol

While all three catalysts show some selectivity to the formation of phenylacetaldehyde, the major product using all is the trimer 2,4,6-tribenzyl-s-trioxane, which was subsequently discovered to be the product of spontaneous polymerisation of phenylacetaldehyde. However, the notable difference between the three catalysts is the time taken for the reaction to reach its completion. The reaction with the Au/TiO$_2$ catalyst takes ~5.5 h while the Au/SWCNT catalysed reaction takes ~3.5 h and finally the Au/P90 reaction takes 4 h (% conversion curves are shown in Figure 3 – supplementary data). Although the aldehyde trimerises to trimer 2,4,6-tribenzyl-s-trioxane, it does not form the carboxylic acid under the aforementioned conditions. This is significant in that it technically means that the catalysts are 100% selective to the aldehyde as the trimer can be hydrolysed back to the aldehyde should it be required. This is done by rapidly heating the trioxane compound at atmospheric pressure which yields pure phenylacetaldehyde as the distillate. This in essence could be described as a clean-up step post oxidation. In order to produce the aldehyde entirely, it is necessary to rapidly heat the product mixture to ~195 ºC to allow distillation of the phenylacetaldehyde to occur within its boiling point range. In addition to affect full distillation, the temperature has to be increased to ~230 ºC to promote decomposition of the trimer to produce the pure aldehyde. The distillation needs to be carried out as quickly as possible to avoid forming further by products, typically higher molecular weight polymers [43, 44].

This is a crude way to produce the aldehyde which is far from ideal when attempting to adhere to the principles of green chemistry. Unfortunately at the reaction conditions chosen and using these catalysts to make the process green, it is not possible to get a 100% conversion to the phenylacetaldehyde under the aforementioned reaction parameters.
3.3.1 Proposed mechanism:

The reaction is thought to occur in three stages. The initial oxidation of the alcohol, which results in the release of hydrogen to form the aldehyde [45]. Then, under excess O₂ and at the reaction temperature of 120 °C approximately three quarters of the aldehyde spontaneously trimerises to 2,4,6-tribenzyl-s-trioxane [44]. The corresponding trimer is more stable than the aldehyde and thus remains predominantly in this form when the reaction reaches its natural conclusion. This is in good agreement with our ¹H and ¹³C NMR results as well as Mass Spectroscopy (results not shown) carried out to clarify the presence of the trimer in the product mixture.

3.4: Aerobic Oxidation of Benzylalcohol

Aerobic oxidation of benzylalcohol was carried out using all three catalysts yielded 100% conversion to the desired benzylaldehyde (% conversion profiles are shown in Figure 4 – supplementary data, reactions in triplicate). Overall, the Au/SWCNT catalyst is the fastest thus the most efficient catalyst for this reaction going to completion in ~3.5 h compared to the Au/TiO₂ catalysed reaction which reaches completion after 7 h and finally the Au/90 catalysed reactions which took 5 h to reach completion. There are no other products formed confirming all three catalysts to be exclusively selective to benzylaldehyde.

In the literature, there are several examples of supported Au catalysts being used to successfully catalyse the selective oxidation of primary alcohols. However, they all either require longer to reach completion, have significantly lower % conversions or require promoters to be effective [45-51].

In addition, in comparison to other selective primary alcohol oxidations recorded in the literature, for example oxidation of benzyl alcohol over supported Au and Pd catalysts reported by Enache, et al [52] as well as the selective oxidation of benzyl alcohol catalysed by Cu (II) in a solvent system reported by Velusamy, et al [53], the three supported Au catalysts used in this work show excellent potential for faster, more efficient selective aerobic oxidation in reaction systems which adhere more closely to the principles of green chemistry.

It is possible that the position of the functional group, in the case of the 2-phenylethanol (β position) and benzylalcohol (α position) plays a part in the substrates ability to be effectively selectively catalysed under these reaction conditions in addition to the differences in the support structures. This is further discussed next.

3.5 Hypothesis for the activity testing findings:

The three composites catalyse the three test reactions in a selective fashion as was hoped. However, there are some unanticipated by products formed, and although potential explanations have been furnished, there now follows a short discussion on alternative possibilities.

Considering the structures of the three reaction substrates, the most obvious difference between them is the position of the functional group on the carbon linker relative to the aromatic ring. The position of the –OH group could have a more activating affect, as it is closer to the ring which could certainly potentially account for the ease with which the 1-phenylethanol and the benzylalcohol are selectively catalysed to their corresponding ketone and aldehyde respectively.

As a consequence, it is possible that steric hindrance could play some part during the 2-phenylethanol oxidation, in which the spontaneous trimerisation of the phenylacetaldehyde product occurred. The 2-phenylethanol substrate is the only one of the three that has its functional group at the β carbon
position relative to the ring. Steric effects have also been known to switch the mechanistic pathway in a catalytic reaction [54-55].

As these reactions are all carried out under mild conditions, perhaps this suggests that there is a strong link between structure and reactivity in these types of compounds under green conditions. This could mean that under these conditions, reactions with substrates having α positioned functional groups are regioselective and not chemoselective, similar to Baeyer-Villiger reactions (oxidation of a ketone to ester or a lactone) and hence the catalysts exhibit higher selectivity because of the position of the migrating group relative to the aromatic ring [56]. In general alcohol oxidations are carried out in solution using reactions in which the hydroxyl hydrogen is replaced by an atom or group that is readily eliminated along with the alpha hydrogen. Examples of these would be Jones’s reagent [57] and pyridinium chlorochromate (PCC) [58]. However, these reactions, although considered mild in terms of how far they take a reaction, are not considered to be green in terms of toxic chemical use and generation. It is likely that a detailed systematic study across a range of aromatic and aliphatic alcohols with substituted functional groups would elucidate more detail regarding these hypotheses.

4: Conclusions

5% by weight Au catalysts were prepared on TiO₂, SWCNT and C and thoroughly characterised. A range of techniques were used for this, SEM/STEM, EDX, XRD, AAS, N₂ physisorption, UV-Vis spectroscopy and Raman spectroscopy. The use of the array of techniques allowed for a detailed and systematic characterisation of the Au nanoparticle morphology, particle size distributions and the metal-support interactions.

SEM showed that Au nanoparticles have a similar size distribution on all supports. XRD confirmed this for the Au/SWCNT and the Au/P90 however, it was inconclusive for the Au/TiO₂ because of the overlap of the anatase phase of the TiO₂ support with the Au nanoparticle Bragg reflections. EDX confirmed the presence of Au on each of the composites while AAS determined the % weight of the Au on the support surfaces. The N₂ adsorption isotherms showed increased surface areas of the composite samples which were expected with the deposition of Au nanoparticles onto crystalline substrates. The SWCNT and P90 supports both showed much larger surface areas than the TiO₂ both before and after deposition which could well lend to their ability to catalyse the oxidation reactions with fast rates alongside the optical and electronic properties of both the supports and the composites. The XRD patterns, EDX spectra and N₂ adsorption isotherms are provided in supplementary information).

In the first stage of the activity testing work, preliminary studies were carried out using the solventless aerobic oxidation of 1-phenylethanol to its corresponding ketone acetophenone using the three catalysts. This reaction has been used previously as a probe reaction for testing new potential catalysts so it served as an ideal model system for this work [23]. The comparison of the novel material, Au NPs supported by SWCNT in the as-synthesised state to more established Au nanoparticle supported catalysts, on TiO₂ and P90 showed that SWCNTs provided a more effective support.

The Au/SWCNT system was seen to catalyse the reaction to completion under green conditions in ~3 h with >95% conversion and 100% selectivity. The Au/TiO₂ and Au/P90 systems also catalyse the reaction but at lower rates and/or selectivity. Using the former, the reaction takes significantly longer and, with the Au/P90, the by-product ethylbenzene is formed. This is likely to be due to surface carbon acting as a reductant during the first reaction cycle. When the Au/P90 catalyst is recycled, the
% conversion to acetophenone increases as expected and the by-product formation ceases. The selective aerobic oxidation of the 2-phenylethanol yielded some unexpected results. All three composites selectively catalyse the reaction to phenylacetaldehyde as expected. However, as phenylacetaldehyde trimerises on standing and so 2,4,6-tribenzyl-s-trioxane was formed alongside the aldehyde. All three catalysts produced very similar reaction profiles with the catalysts all being 100% selective to the aldehyde with ~25% direct conversion to same with no further oxidation to the corresponding carboxylic acid. However, the Au/SWCNT again catalysed the reaction with the fastest rate. In addition, the trimer can be converted back to the aldehyde with relative ease by rapidly heating the reaction mixture produced to affect full distillation. Recycling the catalysts made little difference to the conversion profiles and showed very minimal activity decrease thus highlighting the stability of the catalysts in this type of reaction.

In the third and final test reaction, the selective oxidation of benzylalcohol, all three catalysts show excellent % conversion and % selectivities to benzylaldehyde, the Au/SWCNT again proving to be the most efficient with complete conversion within ~3.5 h compared to ~5 h for the Au/P90 and 7 h for the Au/TiO$_2$ catalysts. No other products were found in these reactions, showing the three catalysts to be exclusively selective to the aldehyde. Recycling the catalysts showed little depreciation in their activity, again illustrating their stability in these reaction styles.

To recapitulate, the results from the solventless aerobic oxidations of the three substrates using the three supported Au catalysts have shown their promise for use in green reactions. From the three, the Au/SWCNT catalyst has been shown to be the most efficient and shows excellent activity and selectivity for green aerobic alcohol oxidations. The thermal stability, tensile strength and surface area of the SWCNT in particular might lend to them being able to be used as catalyst supports across a range of reaction conditions.

Finally it is worth noting that the influence of solution pH on the transport of electrons in an SWCNT system has been shown to directly affect their electrochemical and electrocatalytic properties [13]. This in turn could enhance the selective deposition of the Au NPS onto the SWCNT walls and thus the number of active sites available from the Au/SWCNT system to catalyse the reactions more effectively [17, 21].
5: Appendices:

XRD patterns of TiO$_2$ (dots) and Au/TiO$_2$ (dashes).
XRD Patterns of SWCNT (dots) and Au/SWCNT (dashes)
XRD Patterns of P90 (dots) and Au/P90 (dashes)
EDX Pattern of Au/TiO$_2$
$N_2$ absorption isotherm of TiO$_2$ (dots) and Au/TiO$_2$ (dashes)
N$_2$ absorption isotherm of SWCNT (dots) and Au/SWCNT (dashes)
$N_2$ absorption isotherms of P90 (dots) and Au/P90 (dashes)
UV-Vis Spectra of TiO$_2$ (dots) and Au/TiO$_2$ (dashes)
UV-Vis Spectra of SWCNT (dots) and Au/SWCNT (dashes)

[Inset shows zoomed Au phonon area for Au/SWCNT]
UV-Vis Spectra of P90 (dots) and Au/P90 (dashes)
Raman Spectra of TiO$_2$ (black) and Au/TiO$_2$ (green) at $\lambda_{exc} = 473$nm
Raman Spectra of TiO$_2$ (black) and Au/TiO$_2$ (green) at $\lambda_{exc} = 660$nm
Raman Spectra of SWCNT (dotted) and Au/SWCNT (full) at $\lambda_{exc} = 473$ nm
Raman Spectra of SWCNT (dotted) and Au/SWCNT (full) at $\lambda_{\text{exc}} = 660\text{nm}$
Raman Spectra of P90 (black) and Au/P90 (green) composite samples at $\lambda_{exc} = 473$nm
Raman Spectra of P90 (black) and Au/P90 (green) composite samples at $\lambda_{exc} = 660$nm
6: Acknowledgements: AES would like to thank Dublin Institute of Technology for providing access to instrumentation and for the materials to carry out this work and Dr. Petrica Dulgeru formerly of University College Dublin for TEM imaging.

7: References:


Table 1: Summary of the physical properties of the three gold nanocomposites

<table>
<thead>
<tr>
<th>Composite</th>
<th>% Au (AAS)</th>
<th>d_{Au}(nm) SEM/TEM</th>
<th>d_{Au}(nm) XRD</th>
<th>Surface Area m^2 g^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/TiO₂</td>
<td>5.13</td>
<td>10-20</td>
<td>*</td>
<td>22.79 ± 0.13</td>
</tr>
<tr>
<td>Au/SWCNT</td>
<td>5.21</td>
<td>4-7</td>
<td>4.7</td>
<td>265</td>
</tr>
<tr>
<td>Au/P90</td>
<td>5.42</td>
<td>7-9</td>
<td>5.1</td>
<td>293</td>
</tr>
</tbody>
</table>

* [Bragg reflection overlaps between the anatase phase of TiO₂ and the Au (111), (200) and (311) prevent measurement].
**Table 2: Results for the oxidation of 1-phenylethanol using gold catalysts**

<table>
<thead>
<tr>
<th>Catalyst (mass ratio)</th>
<th>Oxidant</th>
<th>T (°C)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/TiO₂ (1:0.002)</td>
<td>O₂</td>
<td>120</td>
<td>8</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Au/P90 (1:0.002)</td>
<td>O₂</td>
<td>120</td>
<td>4</td>
<td>65*</td>
</tr>
<tr>
<td>Au/SWCNT (1:0.002)</td>
<td>O₂</td>
<td>120</td>
<td>3</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

*Formation of secondary product (ethylbenzene).*
Table 3: Results for the oxidation of 2-phenylethanol using gold catalysts

<table>
<thead>
<tr>
<th>Catalyst (mass ratio)</th>
<th>Oxidant</th>
<th>T (°C)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/TiO₂ (1:0.002)</td>
<td>O₂</td>
<td>120</td>
<td>5.5</td>
<td>~25*</td>
</tr>
<tr>
<td>Au/P₉₀ (1:0.002)</td>
<td>O₂</td>
<td>120</td>
<td>4</td>
<td>~25*</td>
</tr>
<tr>
<td>Au/SWCNT (1:0.002)</td>
<td>O₂</td>
<td>120</td>
<td>3.5</td>
<td>~25*</td>
</tr>
</tbody>
</table>

*Formation of secondary product.
Table 4: Results for the oxidation of Benzylalcohol using gold catalysts

<table>
<thead>
<tr>
<th>Catalyst (mass ratio)</th>
<th>Oxidant</th>
<th>T (ºC)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/TiO$_2$ (1:0.002)</td>
<td>O$_2$</td>
<td>120</td>
<td>7</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Au/P90 (1:0.002)</td>
<td>O$_2$</td>
<td>120</td>
<td>5</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Au/SWCNT (1:0.002)</td>
<td>O$_2$</td>
<td>120</td>
<td>3.5</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>
Figure 1: SEM/TEM images of (i) Au/TiO$_2$ (ii) SWCNT (iii) Au/SWCNT* and (iv) Au/P90
Figure 2: Conversion of 1-Phenylethanol to Acetophenone (reactions in triplicate) using O$_2$ over (i) Au/TiO$_2$ (ii) Au/SWCNT and (iii) Au/P90* (dashed graphs show ethylbenzene conversion).
Figure 3: Conversion of 2-Phenylethanol to Phenylacetaldehyde (reactions in triplicate) using O₂ over (i) Au/TiO₂ (ii) Au/SWCNT and (iii) Au/P90.
Figure 4: % Conversion profiles for the aerobic oxidation of Benzylalcohol to benzyaldehyde over O₂ (i) Au/TiO₂ (ii) Au/SWCNT and (iii) Au/C