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Suzuki Coupling Activity of an aqueous phase Pd nanoparticle dispersion and a Carbon Nanotube/Pd nanoparticle composite.

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Abstract

An aqueous phase dispersion of Pd nanoparticles stabilised by 4-Dimethylaminopyridine (DMAP) promotes model Suzuki coupling reactions. The dispersion contains Pd nanoparticles of 3.4±0.5 nm and a Pd(II) species ($Pd(DMAP)_4(OH)_2$) which forms following aerobic oxidation of the nanoparticles.

The activity of the nanoparticle dispersion in promoting the Suzuki reactions is directly proportional to the size of the halogen on the substrate (as is usual for these coupling reactions) and also to the age of the nanoparticle dispersion.

The $Pd(DMAP)_4(OH)_2$ complex can be isolated from the dispersion and is found to be very active in promoting the reactions. Its formation following aerobic oxidation of the nanoparticles is proposed as the reason for the improved activity of the dispersion with age.

The nanoparticles present in the dispersion can, through displacement of the stabilising ligand, be immobilised onto functionalised Multi Wall Carbon Nanotubes (MWCNT) and the composite formed is an active and recyclable catalyst. This MWCNT/Pd-DMAP NP composite acts as a reservoir of dissolved Pd species, which function as homogeneous catalysts under reaction conditions.

Keywords: Suzuki Reaction, Pd nanoparticles, Multi Wall Carbon Nanotube.

Introduction

Many different types of transition metal nanoparticles have been used to catalyse a variety of synthetic chemical reactions including the Hydrogenation, Heck, Suzuki, Sonagashiri and Stille reactions [1-4]. Progress in the field has been rapid with a multitude of reactions now known to be catalysed by nanoparticles stabilised by a variety of surfactants [5], thiols [6], polymers (PVP, etc) [7-9] and dendrimers [10-13]. Interestingly, Pd nanoparticles prepared by different methods and using different stabilising ligands, *e.g.* thiol [14], PVP [15, 16], and dendrimers [17] are also known to be susceptible to oxidation into dissolved ionic Pd(II) species.

Therefore, nanoparticles with similar types of stabilisers are known to (a) be used in catalytic reactions and (b) undergo oxidation. It is therefore not unreasonable to suggest that some reactions catalysed by palladium nanoparticles stabilised with thiol, PVP and dendrimers may unwittingly have had some oxidised species present prior to the start of the reaction, and furthermore it is not unreasonable to suggest that these oxidised species may contribute to (or cause) the catalysis attributed to the nanoparticles. It is conceivable that in a palladium nanoparticle dispersion the presence of oxidised species and their subsequent roles in the catalytic process may have gone unnoticed due to difficulties in the detection and characterisation of trace amounts of these species.

A case in point is the recent report published by Turkenburg *et al.*, [18] which evaluated the catalytic activity of DMAP stabilised palladium nanoparticles incorporated in polyelectrolyte microcapsule shells for a Sonagashiri cross-coupling reaction. The DMAP stabilised palladium nanoparticles used by Turkenburg *et al.* were prepared using the phase transfer procedure outlined by Caruso [19].

Recently, [20] we have identified previously undocumented Pd(II)/DMAP complex species present within this particular nanoparticle preparation. Therefore it is probable that these Pd(II)/DMAP complex species were also unknowingly present in the polyelectrolyte microcapsules used by these workers to catalyse the Sonagashiri reaction. However, the authors did not discuss these complex species or any possible role in the observed catalytic activity.

Previous work within our group has also described the one-phase preparation of an aqueous dispersion of DMAP stabilised palladium nanoparticles [20]. Following detailed characterisation the presence of oxidised Pd(II)/DMAP complex species were also identified within this dispersion. Oxidation of the DMAP stabilised palladium nanoparticles in air led to the formation of these species. Despite the presence of these species, the nanoparticles remain dispersed and still exist as individual entities for several months, facilitating an assessment of their catalytic activity.

In terms of Pd catalysed processes the Suzuki reaction is of particular interest. The reaction is proving to be an extremely important method for the construction of unsymmetrical biaryl compounds (which are found in pharmaceuticals, herbicides, natural products, conducting polymers, molecular wires and liquid crystals [21]) and has found wide applications in organic synthesis [22, 23].

Dissolved Pd complexes are generally the homogeneous catalysts used in these reactions (at concentrations of ~ 2 mol%) but there is an obvious benefit, both in terms of catalyst re-cyclability and cost, in the use of heterogeneous (or hetrogenised) catalysts [24, 25].

It is in this context that this work assesses the catalytic activity of the DMAP stabilised palladium nanoparticle dispersion, prepared and characterised previously [20], in aqueous model Suzuki reactions. The role which the Pd(II)/DMAP complex species, formed following the oxidation of the nanoparticles, play in the observed catalytic activity of the dispersion, will also be assessed.

Furthermore, the labile nature of the DMAP stabilising molecule at the surface of the nanoparticles permits the immobilisation of the palladium nanoparticles onto thiolated Multi-Walled-Carbon-Nanotubes (MWCNTs) resulting in the formation of a recyclable composite. The catalytic activity and recyclability of this composite is also assessed in aqueous model Suzuki reactions.

Experimental

All chemicals were used as supplied by the Sigma-Aldrich Chemical Company Ltd or Reagecon, unless otherwise stated. The water used in all experiments was distilled deionised Millipore-MilliQ water (18 MΩ cm^{-1}).

Catalyst Preparation

Nanoparticle dispersions were prepared as previously reported [20]. Briefly, Na_2PdCl_4 (37.3 mg, 0.127 mmol) was dissolved in distilled-deionised water (3 mL) and stirred vigorously. 4-Dimethylaminopyridine (DMAP) (83.3 mg, 0.682 mmol) was sonicated into distilled-deionised water (9 mL) and added to the stirring solution. The resulting mixture was stirred for 20 minutes during which time a colour change from an orange/yellow colour to a clearer pale yellow colour was observed.

The pale yellow solution was reduced by the addition of $NaBH_4$ (1% w/v, 1.100 mL) in 0.100 mL aliquots. A colour change from pale yellow to black was observed immediately. The resulting DMAP stabilised palladium nanoparticles were stirred vigorously for a further 30 minutes. TEM analysis has shown that the particles have a mean diameter of 3.4±0.5 nm and remain dispersed in solution as individual entities for periods of more than 6 months [27].

Thiol-Modified Multi-Walled Carbon Nanotubes (MWCNTs), prepared by a carbon arc discharge method, were supplied by the MER Corporation. The MWCNTs were functionalised via an amide coupling reaction using a slightly modified procedure to that described by Sainsbury *et al.* [26].

As-received MWCNTs (0.003 g) were suspended in nitric acid (3 mL, 70% w/w) by sonication (15 minutes). The resulting black suspension was refluxed for 24 hours at 130 °C and allowed to cool to room temperature. The suspension was then filtered through a polycarbonate membrane filter (Whatman-UK, 0.2 µm pore diameter) and washed with deionised-distilled water (1 L).

The MWCNTs retained on the membrane filter were suspended in deionised-distilled water (10 mL) by sonicating the filter membrane (10 minutes). $KMnO_4$ (0.009 g, 5.696 x 10^{-5} mol) was added and the resulting dark-purple suspension cooled in an ice bath to 0 °C under magnetic stirring for 1 hour. $HClO_4$ (3 mL, 70% w/w) was added to the solution, which was stirred at room temperature for 1 hour. Citric acid monohydrate (0.186 g, 8.851 x 10^{-4} mol) was added and the suspension was stirred until it became grey in colour. The resulting suspension of MWCNTs was filtered through a polycarbonate membrane filter (Whatman-UK, 0.2 µm pore diameter) and washed with deionised-distilled water (1 L).

The retained MWCNTs were suspended in deionised-distilled water (10 mL) through sonication of the filter membrane. DMAP (0.003 g, 2.456 x 10^{-5} mol,) and 1-(3-Dimethylaminopropyl)-3-Ethyl-Carboiimide Hydrochloride (EDAC) (0.191 g, 9.963 x 10^{-3} mol) were added and stirred for 10 minutes. 2-mercaptoethylamine hydrochloride (0.050 g, 4.401 x 10^{-4} mol) was added and the resulting suspension stirred for 24 hours at room temperature. The suspension of MWCNTs was filtered through a polycarbonate membrane filter (Whatman-UK, 0.2 µm pore diameter) and washed with deionised-distilled water (1 L). The retained MWCNTs were again suspended in deionised-distilled water (10 mL) by sonication and were ready for use. See Figure 1(a) for a schematic showing these reactions.

MWCNT/Pd-DMAP NP composites, *i.e.* Multi-Walled-Carbon-Nanotube/DMAP Stabilised Pd Nanoparticle composites were prepared by the addition of a known amount of DMAP stabilised palladium nanoparticle dispersion to thiol-modified multi-walled-carbon-nanotubes [27].

Previous work [20, 27] has shown that the DMAP stabilizing ligand can be easily removed from the Pd nanoparticles and replaced with a thiol ligand. We have used this chemistry to immobilize the nanoparticles onto the thiol-modified MWCNTs.

In a typical composite preparation, 1 mL of the prepared thiolated MWCNTs were sonicated for 5 minutes and the DMAP stabilised palladium nanoparticle dispersion (64 μL of a 887 ppm Pd dispersion) was added with brief mixing. The composite was kept in solution through periodic sonication. After 12 hours it was allowed to fully precipitate, the resulting clear supernatant was carefully removed and distilled-deionised water (1 mL) was added followed by sonication for 10 seconds.

This subsequent MWCNT/Pd-DMAP NP composite solution was filtered through a polycarbonate membrane filter (Whatman-UK, 0.2 μm pore diameter) and the retained composite was washed with a further 100 mL of distilled-deionised water. The composite was removed from the membrane by sonication into 5 mL of distilled deionised water and was ready for use. An aliquot of the resulting MWCNT/Pd-DMAP NP composite (10 μL) was deposited on a carbon-coated copper grid and was characterised by TEM. The average Pd nanoparticle size, as measured by TEM, is 3.6±0.6 nm. Figure 1 gives a schematic of the composite preparation procedure, a typical TEM of the dispersion composite and a histogram showing the Pd nanoparticle size distribution.

Note: All Transmission Electron Microscopy (TEM) images were recorded using a JEOL JEL-2000 EX electron microscope with a lattice resolution of 0.14 nm and a point-to-point resolution of 0.3 nm operating at 80 kV. Samples were prepared by evaporating a drop of the appropriate dispersion onto the surface of a carbon-coated 400 square mesh copper TEM grid.

Catalysed Suzuki Reactions

The aqueous phase Suzuki reactions between Phenylboronic acid and 4-Iodobenzoic acid, 4-Bromobenzoic acid or 4-Chlorobenzoic acid (see Figure 2) were catalysed using three different types of Pd catalyst. These involved (1) the DMAP stabilised palladium nanoparticle dispersion, (2) the $Pd(DMAP)_4(OH)_2$ complex crystals isolated from the nanoparticle dispersion [20] and (3) the Multi-Walled-Carbon-Nanotube / DMAP stabilised Pd nanoparticle composite.

<u>(1) Suzuki Reactions catalysed by DMAP Stabilised Pd Nanoparticle Dispersions</u>. In a typical procedure, sodium carbonate (318 mg, 3.0 mmol), 4-Iodobenzoic acid (248 mg, 1.0 mmol) and Phenylboronic acid (121.9 mg, 1.0 mmol) were dissolved in distilled-deionised water (30 mL) with brief sonication. The Pd nanoparticle dispersion (64 μL, 0.05 mol%) was added and nitrogen was bubbled through the reaction mixture for 5 minutes. The reaction mixture was refluxed at 100 °C under nitrogen for 10 minutes with stirring. The reaction mixture was cooled and then acidified from pH 9 to pH 1 using aqueous sulphuric acid. The product was extracted

by washing with 3 x 30 mL aliquots of chloroform and subsequently the % yield was analysed using ^{1}H NMR. The exact same procedure was utilised for the 4-Bromobenzoic acid (201.0 mg, 1.0 mmol) reactions. The 4-Chlorobenzoic acid (156.6 mg, 1.0 mmol) reactions used the same general procedure except the reactions were refluxed for 6 hours instead of 10 minutes and a larger amount of Pd nanoparticle dispersion (480 μL, 0.40 mol%) was added. It is well known that the rate of Suzuki reactions is directly proportional to the size of the halogen atom, *i.e.* I > Br > Cl [28] and thus more forceful conditions were required for the Chloro-substituted substrates.

(2) Suzuki Reactions catalysed by the $Pd(DMAP)_4(OH)_2$ Complex.

The same general procedure was used as above except isolated $Pd(DMAP)_4(OH)_2$ complex crystals were used to catalyse the reactions instead of the DMAP stabilised palladium nanoparticle dispersion. The complex crystals were dissolved in water prior to the commencement of the Suzuki reactions. 6-hour reaction times were again used for the 4-Chlorobenzoic acid reactions (with 5.8×10^{-2} mol% Pd) while 10 minutes reaction times were still used for the 4-Iodobenzoic acid and 4-Bromobenzoic acid reactions (using 4×10^{-3} and 1.3×10^{-2} mol% Pd respectively). Due to the increasing difficulty of promoting the reaction as the size of the halo- substituent decreases different mol% of Pd complex were used in order to achieve measurable conversions of reactant to product.

(3) Suzuki Reactions catalysed MWCNT/Pd-DMAP NP Composite.

The same general procedure was used as stated in (1) above except MWCNT/Pd-DMAP NP composite was used to catalyse the reactions instead of the DMAP stabilised palladium nanoparticle dispersion. The reactions, which were also carried out under reflux conditions, were studied predominantly using the 4-Iodobenzoic acid substrate. 2-hour reaction times were used and 0.04 mol% (based on Pd concentration) composites were used as catalysts. The composite was removed from the reaction mixture prior to extraction of the product.

The MWCNT/Pd-DMAP NP composite could be repeatedly recycled from completed Suzuki reactions following filtration of the cooled reaction mixture through a polycarbonate membrane filter (Whatman-UK, 0.2 µm pore diameter).

Yield Analysis.

To estimate the yield of the reactions ^{1}H NMR was used. All proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded using a Varian 300 MHz FT-NMR spectrometer and 4,4 Dimethoxybiphenyl was used as an internal standard. Following work up of the reaction, the internal standard (214.3 mg, 1.0 mmol) was added to the extracted chloroform product layer. The final volume was made up to 200 mL using chloroform and sonicated briefly. A representative sample of 5 mL of the chloroform layer was dried under vacuum at room temperature for 5 minutes and a subsequent ^{1}H NMR spectrum obtained in $CDCl_3$. The product yield was analysed (following construction of appropriate calibration plots) by comparison of the integration for the product resonance at δ 8.17-8.20 and the integration for the reference standard resonance at δ 6.94-6.97 in the ^{1}H NMR spectra using Mestrec software.

It should be noted that GC analysis was also used to confirm the results obtained following ^{1}H NMR yield analysis and the results always agreed within ±3%. Formation of the possible by-product biphenyl was not observed.

Results and Discussion

Activity of nanoparticle dispersion.

As a probe for Pd impurities in the reactants, a test reaction in the absence of catalyst was performed. This reaction showed no conversion under reaction conditions after 24 hours. Thus, any reactivity in the presence of the nanoparticle dispersions must be due to the catalytic activity of these dispersions.

Figure 3 shows the % conversion of the 4-Chloro-, Bromo- and Iodo- substituted benzoic acids to product when catalysed by various concentrations of the nanoparticle dispersions (see experimental section and figure legend for details).

The first point to note is that it is clear that all the reactions (to greater or lesser extents) are promoted by the presence of the nanoparticle dispersions. Obviously the reaction proceeds more rapidly in the case of the 4-Iodo substituted substrate while the 4-Chloro substituted material needs the most forceful conditions to achieve a reasonable conversion.

While the measured conversion of the 4-Chloro substituted substrate is higher than that of the 4-Bromo material it should be noted that the conditions of reaction in the latter case are far more forceful, *i.e.* 8 times more catalyst used and a reaction time 36 times longer than was used in the 4-Bromo case.

It should be noted that the dispersions used during these catalytic reactions were all aged for 1 hour prior to commencement of the reactions. In previous work [20] we have noted that after prolonged exposure to air ^{1}H NMR characterisation of the dispersions showed the development of resonances which have been shown to be due to the formation of oxidised Pd containing species. The formation of these species obviously increases as a function of time. To attempt to understand the effect that nanoparticle dispersion aging and the presence of these species might have on the catalytic activity of the dispersions a series of activity measurements were performed for each of the various substrates at different times following the nanoparticle dispersion preparation (specifically 1h, 25h, 4 days, 16 days and 25 days following preparation).

Figure 4 shows the trends in reactivity seen in the promotion of the 4-Iodo-, 4-Bromo- and 4-Chloro-benzoic acid reactions with phenylboronic acid as a function of nanoparticle dispersion age. A longer reaction time and higher concentration of catalyst were used when studying the 4-Chloro reaction.

It can clearly be seen that the activity of the dispersions in promoting the desired reaction generally increases with the age of the nanoparticles. This is most evident from the data relating to the 4-Bromo reaction, increasing from ~ 20% conversion using the 1 hour old dispersion to over 90% conversion when the dispersion is 10 days old. The % conversion of reactants into products during the reaction of 4-Iodo benzoic acid increases from ~ 88% to over 95% when the dispersion is aged from 1 hour to 4 days. In the case of the 4-Chloro reaction the % conversion increases with the age of dispersion (except in the case of one data point) from ~43% (from a 1 hour old dispersion) to ~ 55% for a dispersion that was 16 days old).

Therefore we can state that something takes place within the dispersion as it ages which results in the formation of a more active catalyst for the promotion of the Suzuki Reaction. Previously ^{1}H NMR characterisation [20] clearly showed the formation of oxidised Pd(II) species in the nanoparticle dispersion that were not detectable using either UV-Vis spectroscopy (to monitor their formation) or using TEM (to monitor the destruction of the nanoparticles). These Pd(II) complexes were thus an obvious candidate for the active species which evolved during the aging of the nanoparticle dispersions.

Activity of $Pd(DMAP)_4(OH)_2$ complex

In order to determine whether these Pd(II) complexes are the active species evolved during the aging of the nanoparticle dispersions, one complex (a square planar $Pd(DMAP)_4$ ion coordinated to two OH^- counter ions), which could be isolated from the aged dispersions [20] was used as a catalyst to promote the reactions of interest.

Different amounts of this complex were used to catalyse the 4-Halo Suzuki reactions (see experimental section) and again it was seen that reaction to product took place in each case. In the case of the 4-Iodo substrate 87% of the reactants were converted during the 10 minute reaction (using 0.004 mol% complex in the mixture) while in the case of the 4-Bromo substituted analogue (using ~ 4 times the mol% of complex and the same reaction time) 53% conversion was seen. Again the 4-Chloro reaction proved the most difficult to catalyse but in any case following a 6 hour reaction using ~ 16 times as much catalyst as was the case for the 4-Iodo reaction 24% conversion was seen. It is clear therefore that the complex (even when present at a Pd concentration an order of magnitude lower than the Pd nanoparticle promoted reactions discussed above) is still an efficient catalyst for the promotion of the Suzuki reactions.

Interestingly de Vries *et al.* have identified the catalysis of Heck and Suzuki reactions using extremely low palladium acetate catalyst loadings, which they dubbed "homeopathic" ligand free palladium catalysts [29-31]. They reported that the Suzuki reaction of aryl bromides were catalysed in high yields using 0.02-0.05 mol% palladium and even the reactions of some aryl chlorides were catalysed using 0.005-0.05 mol% palladium. Comparison of the low amounts of catalyst used here for the 4-Iodobenzoic acid and 4-Bromobenzoic acid reactions with the amounts used by de Vries *et al.* would indicate that the $Pd(DMAP)_4(OH)_2$ complex could also be considered to be in this category of catalyst.

In order to analyse whether the nanoparticles or the formed complexes contribute the majority of the catalytic activity of the dispersions it was decided to attempt to immobilise the nanoparticles onto a solid support. It was envisaged that this would not only facilitate the recycling of the nanoparticles from the reaction medium but could also lead to the eventual removal of any contributions from the complex species to the observed catalytic activity. The reaction between 4-Iodobenzoic acid and phenylboronic acid was used as a probe reaction to ascertain whether the MWCNT/Pd-DMAP NP composite promotes the Suzuki reactions.

Recyclable activity of MWCNT/Pd-DMAP NP composite and influence of Pd(DMAP)$_4$(OH)$_2$ complex.

MWCNT/Pd-DMAP NP composite was prepared as outlined in the experimental section. It is possible, indeed probable, that this composite contains an amount of immobilised Pd(II) complexes as well as the desired immobilised particles. In order to analyse the influence of these Pd(II) complexes on the activity of the MWCNT/Pd-DMAP NP composite a MWCNT_Complex composite was also prepared by adding Pd(DMAP)$_4$(OH)$_2$ complex to thiolated MWCNTs using the same general procedure as that outlined to prepare the MWCNT_Pd-DMAP NP composite (see experimental section) including all washing steps. This MWCNT_Complex composite contained a Pd loading equivalent to a 0.05 mol% catalyst loading within the reactant mixture. It should be noted that a control reaction using thiolated MWCNTs failed to produce the 4-Biphenylcarboxylic acid product even after a 24 hour reaction time showing that any reactivity in the presence of these composites must be exclusively due to the catalytic activity of the composites.and not the thiolated MWCNTs.

Figure 5 shows the % conversion obtained in the model Suzuki reaction using the MWCNT/Pd-DMAP NP composite and the MWCNT_Complex composite. Only two reactions of the latter material were carried out (the % conversion obtained using the MWCNT_Complex composite decreased from 100% to 20% following one recycle of the catalyst) while the MWCNT/Pd-DMAP NP composite catalyst was used for five reaction cycles.

It is clear from Figure 5 that the composite prepared using Pd(II) complex (MWCNT_Complex composite), while being active in the first reaction, does not maintain a significant activity after recycling. This is probably due to the removal of the $Pd(DMAP)_4(OH)_2$ complex from the thiolated MWCNT material during the course of the 1st reaction. On the other hand the MWCNT/Pd-DMAP NP composite catalyst retains a significant proportion of its catalytic activity through all reaction cycles. Assuming that any $Pd(DMAP)_4(OH)_2$ complex present on the MWCNT/Pd-DMAP NP composite is totally removed following the first two or three cycles of the catalyst (as is suggested from the reactions catalysed by the MWCNT_Complex composite) then all further activity must be derived from the Pd nanoparticles immobilised on the MWCNT surface. This would initially suggest that the surface of the Pd nanoparticles can catalyse the reaction.

However, further TEM analysis of the recycled MWCNT/Pd-DMAP NP composite shows a further aspect of interest within this reaction mixture. TEM (shown in figure 6) shows that the Pd nanoparticles sinter (increasing their mean size to 7.4±1.9nm) during the reactions. It should be recalled that the temperature of reaction was 100 °C which is significantly below any temperature where thermal sintering of the Pd would be expected to take place. Therefore we conclude that the reason for sintering involves a reaction cycle where Pd atoms are removed (following suitable complexation with elements of the reaction medium) from the nanoparticles and travel into solution (where they presumably act as efficient Suzuki catalysts). Subsequently, as the reaction mixture is cooled before being filtered to remove the composite, the Pd species re-deposit onto the nanoparticle catalyst. This gives the Pd nanoparticles an opportunity to ripen with some nanoparticles dissolving and others becoming larger in an Ostwald ripening process.

It should be recalled that the mechanism of the homogeneously catalysed Suzuki reaction involves Pd(II) and Pd(0) intermediates [32] which are formed following oxidative addition and reductive elimination reactions respectively. It is probable that the formation of these species can also be related to the removal and re-deposition of Pd atoms onto the nanoparticles and thus contribute to the ripening process.

As an aside, when the MWCNT/Pd-DMAP NP composite is used in the promotion of the 4-Bromobenzoic acid and 4-Chlorobenzoic acid Suzuki coupling reactions measured conversions are not as high as above and sintering of the Pd nanoparticles is not observed. This suggests that under these conditions the concentration of dissolved Pd species present during these reactions is not as high as when the 4-Iodobenzoic acid substrate is used. This in turn suggests that the 4-Iodobenzoic acid molecules have some role to play in the dissolution (and activation) of the Pd nanoparticle based catalyst.

In order to test this hypothesis (*i.e.* that active dissolved Pd species are present in the reaction solution when MWCNT/Pd-DMAP NP composites are used as catalysts) we attempted to analyse, using different techniques whether dissolved Pd entered the reaction solution during the course of the reaction.

The reaction between 4-Iodobenzoic acid and phenylboronic acid was repeated using fresh MWCNT/Pd-DMAP NP composite and the catalyst was recycled using hot filtration through five 2 hour reactions. Following this, a sixth reaction was carried out for 2 hours and this reaction mixture was also filtered while hot through a polycarbonate membrane filter (Whatman-UK, 0.2 µm pore diameter). These several reaction cycles were used in order to ensure that any Pd(DMAP)$_4$(OH)$_2$ complex present in the initial nanoparticle dispersion was fully removed from the catalyst. It is noted from above that one reaction cycle was sufficient to remove significant catalytic activity (and presumably Pd complex) from the MWCNT_Complex compositeand it was assumed that the three further reaction cycles would be sufficient to ensure that all of the Pd(II) complexes are removed from the MWCNT/Pd-DMAP NP composite. The purpose of the hot filtration especially on the sixth rection cycle was to prevent the re-deposition of any dissolved Pd species which is believed to take place as the mixture cools. An aliquot of this sixth reaction solution was then submitted for AA analysis but the levels of Pd in solution (if any) were below the detection limit of the AA spectrometer.

A further portion of this solution was analysed for % conversion to product (18% under these conditions). A final portion of this liquid was subsequently refluxed in the presence of fresh reactants (but in the absence of any freshly added catalyst) for a further 2 hours. Following this, the mixture was again analysed for % conversion and it was found that this had increased to 31%.

Previously we have shown that the reaction did not proceed in the absence of catalyst, therefore this result proves that there must be a small amount (below the detection limit of Atomic Absorbance Spectroscopy which in our instrument is reported at 10ng/mL) of Pd present within the reaction mixture and that this material is capable of catalysing the Suzuki reaction (albeit using extended reaction times).

Thus, it seems that the one manner in which the recyclable MWCNT/Pd-DMAP NP composite performs as a catalyst for the Suzuki reaction is by acting as a reservoir for dissolved Pd species which can act as the "true" catalyst for the reaction. Whether the surface of the Pd nanoparticles in the initial dispersion or the nanoparticles deposited on the MWCNT support contributes significantly (or in any way) to the reaction mechanism is as yet unclear.

Conclusions

DMAP stabilised Pd nanoparticle dispersions catalyse the Suzuki reaction between three 4-Halobenzoic acids and phenylboronic acid. Oxidised Pd(II) complexes present within the dispersion, specifically $Pd(DMAP)_4(OH)_2$, are extremely active catalysts for the reaction. These species form through reaction of the nanoparticles with O_2 and thus their concentrations increase within the dispersion as a function of time. Therefore, older nanoparticle dispersions are more active catalysts for the promotion of the Suzuki reactions than freshly prepared dispersions.

The Pd nanoparticles can be immobilised onto Multi Walled Carbon Nanotubes to form a recyclable composite catalyst through a ligand exchange process whereby DMAP is displaced by thiol molecules chemically attached to the MWCNT surfaces.

The resultant MWCNT/Pd-DMAP NP composite is also active in the promotion of the reaction of interest although it seems that the immobilised nanoparticles act as reservoirs for dissolved Pd species that are the “true” Suzuki catalysts. The concentration of these Pd species dissolved in the reaction medium following six reaction cycles, while being sufficient to promote small amounts of conversion over an extended period of time, is below the detection limits of AA spectroscopy.

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Figure Legends

Figure 1: (a) Schematic of preparation procedure used to produce MWCNT/Pd-DMAP NP composite material (b) TEM of resultant composite material (c) histogram showing nanoparticle size distribution. See text for details.

Figure 2: Suzuki reaction of interest between phenylboronic acid and 4-Halobenzoic acids.

Figure 3: Conversions of Chloro-, Bromo-, and Iodo- substituted substrates in the Suzuki reaction promoted by Pd nanoparticle dispersions. I and Br substituted benzoic acid: 0.05 mol % Pd and 10 min. reaction, Cl substituted benzoic acid: 0.4 mol% Pd and 6 h reaction. The nanoparticle dispersions were aged for 1h prior to the beginning of the reaction.

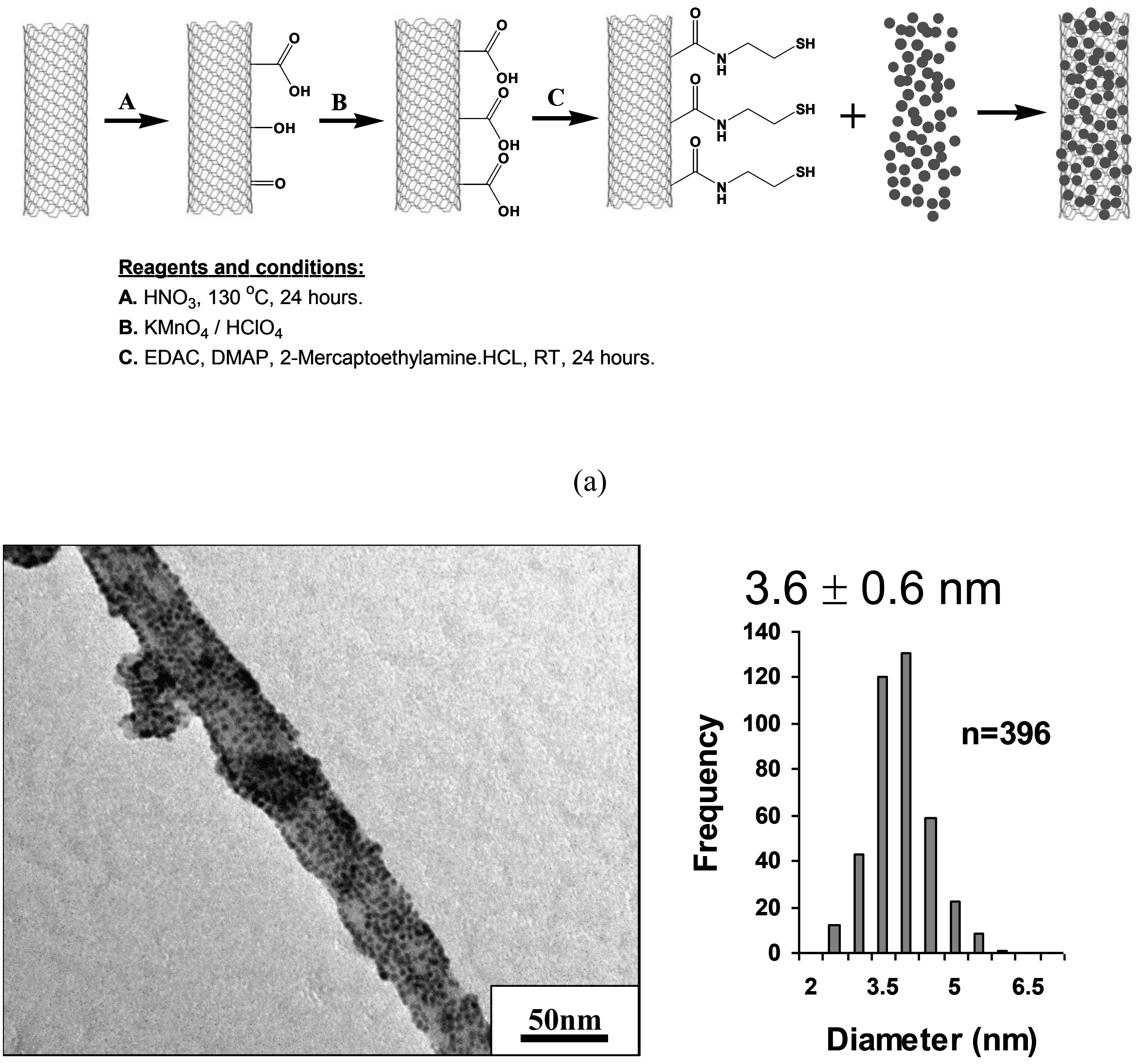
Figure 4: Plot of % conversions of Chloro- (▲), Bromo- (●), and Iodo- (■) substituted substrates in the Suzuki reaction promoted by Pd nanoparticle dispersions as a function of the age of the nanoparticle dispersion. I and Br substituted benzoic acid: 0.05 mol % Pd and 10 min. reaction, Cl substituted benzoic acid: 0.4 mol% Pd and 6 h reaction.

Figure 5: Plot showing the activity of the MWCNT/Pd-DMAP NP compositecatalyst (■) and MWCNT_Complex composite catalyst(▲) in promoting the reaction between 4-Iodobenzoic acid and phenylboronic acid.

Figure 6: (a) TEM and (b) histogram showing the average Pd nanoparticle size on the MWCNT/Pd-DMAP NP composite following catalysis of the Suzuki reaction between phenyl boronic acid and 4-Iodo-benzoic acid. Note the average nanoparticle size has increased from ~ 3.6 ± 0.6 nm (see Figure 1) to ~ 7.4 ± 1.9 nm.

Figures

Figure 1



Reagents and conditions:
A. HNO_3, 130 °C, 24 hours.
B. $KMnO_4$ / $HClO_4$
C. EDAC, DMAP, 2-Mercaptoethylamine.HCL, RT, 24 hours.

(a)

(b)

(c)

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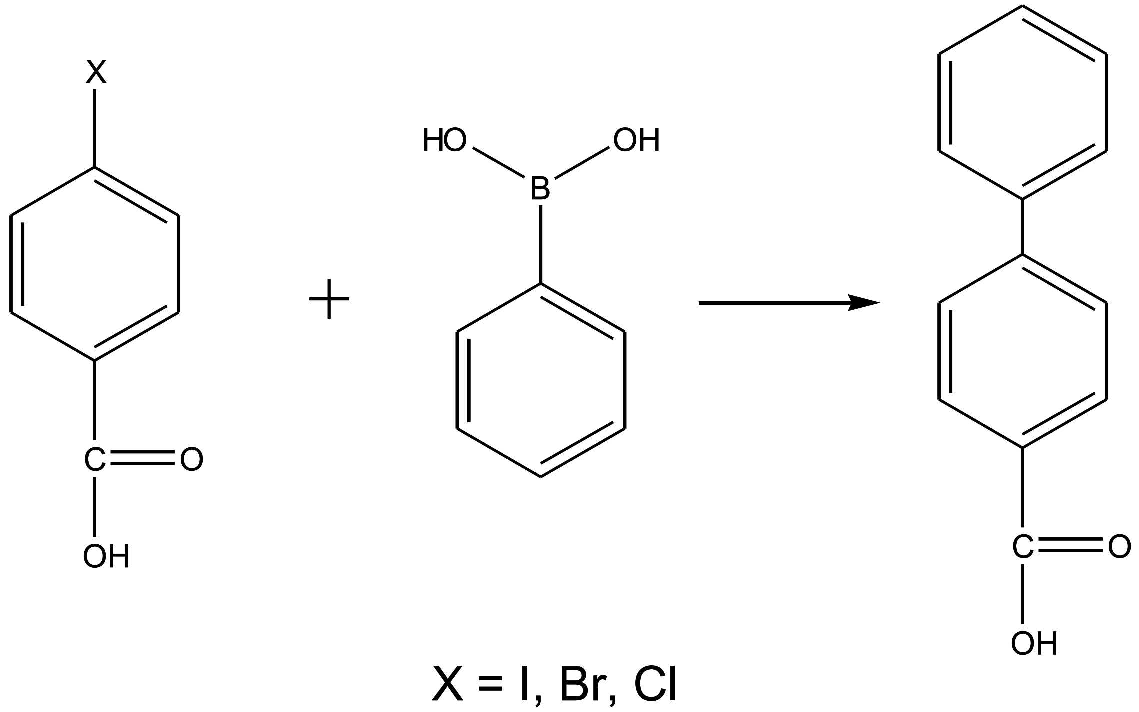
Figure 2



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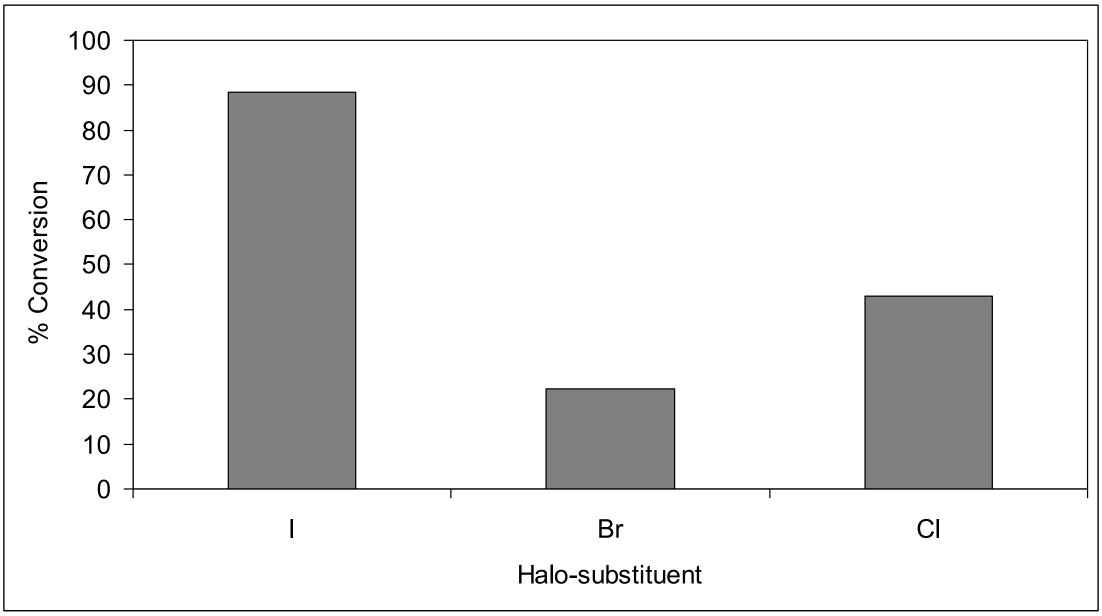

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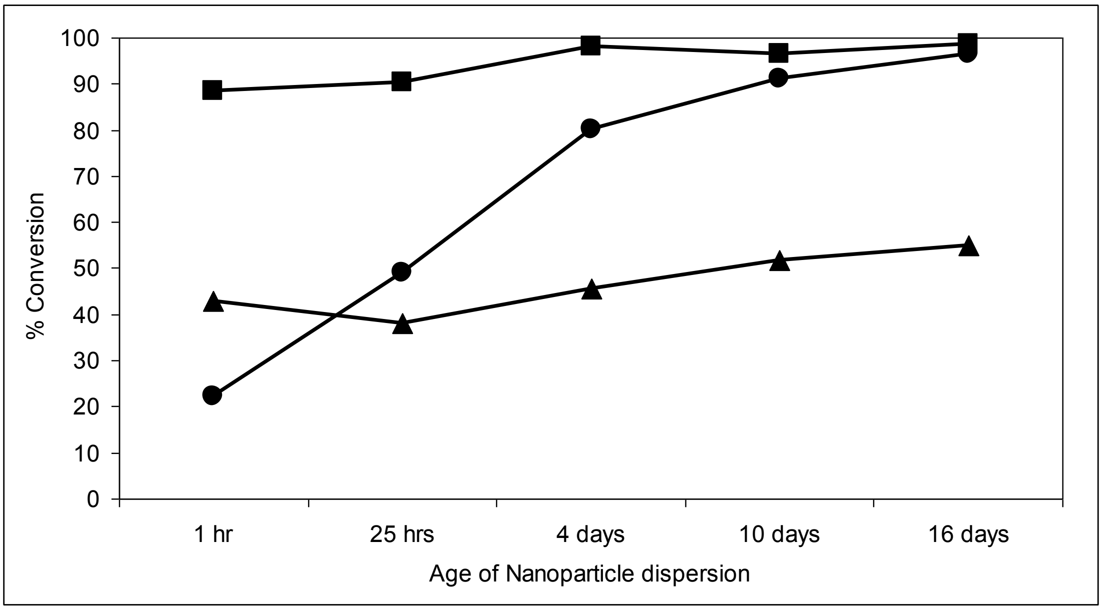

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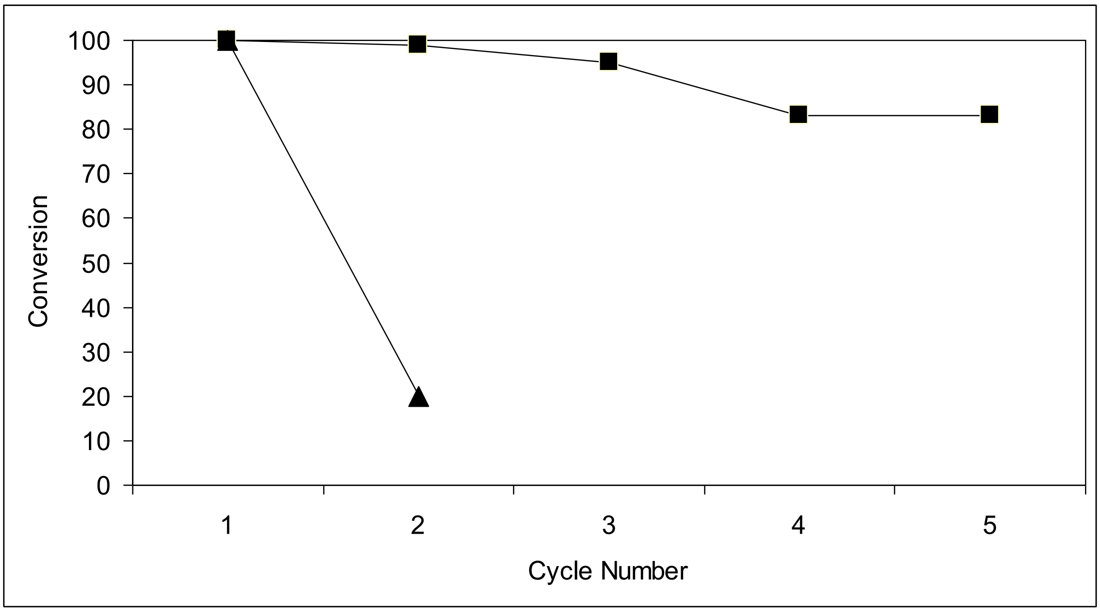

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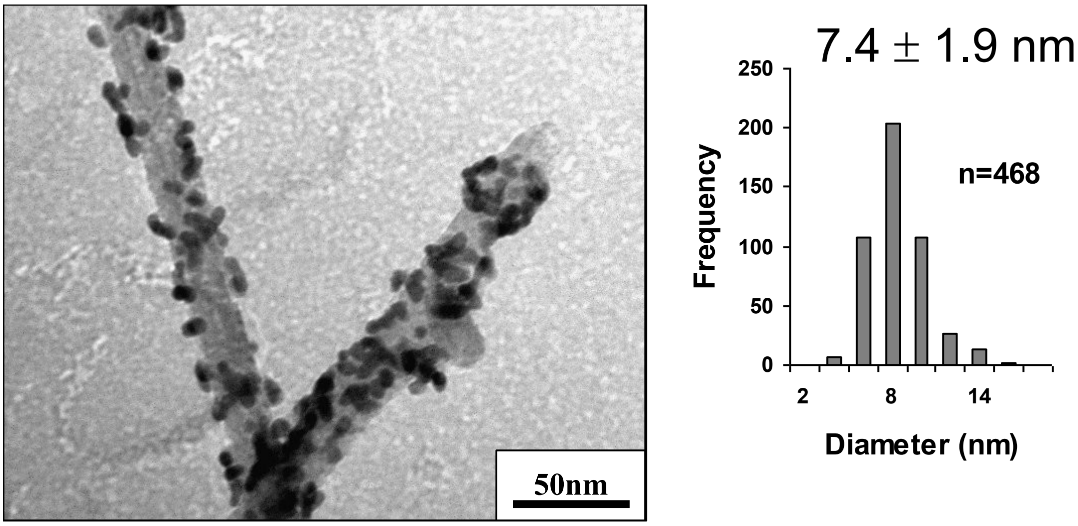

(a) (b)

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