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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-walled carbon nanotubes (MWCNTs) and the composite formed is an active and recyclable catalyst. The MWCNT/Pd-DMAP NP composite acts as a reservoir of dissolved Pd species, which function as homogeneous catalysts under reaction conditions.

1. 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 and Gittins [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

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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 heterogenised) 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.

2. Experimental

2.1. Catalyst preparation

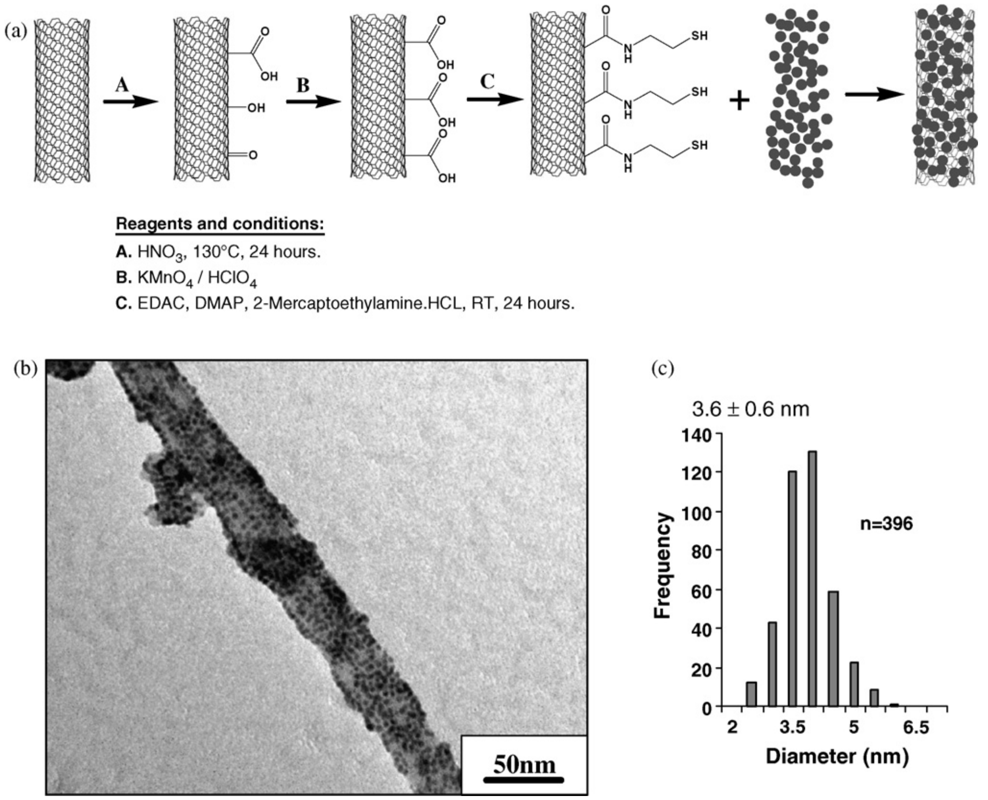
Nanoparticle dispersions were prepared as previously reported [20]. Solutions of Na_2PdCl_4 and 4-dimethylaminopyridine (DMAP) were mixed and stirred for 20 min during which time a colour change from an orange/yellow colour to a clearer pale yellow colour was observed.

The pale yellow solution was reduced by the addition of $NaBH_4$ and the resulting DMAP stabilised palladium nanoparticles were stirred vigorously for a further 30 min. 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 [20].

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 and Fitzmaurice [26]. The nanotubes were treated in sequence with HNO_3, $KMnO_4$, $HClO_4$ and citric acid. Subsequently they were treated with DMAP and 1-(3-dimethylaminopropyl)-3-ethyl-carboiimide hydrochloride (EDAC) and 2-mercaptoethylamine hydrochloride. See Fig. 1(a) for a schematic showing these reactions. The detailed method for their production has been reported previously [27].

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] has shown that the DMAP stabilizing ligand can be easily removed from the Pd nanoparticles and replaced with a thiol ligand.

In a typical composite preparation, thiolated MWCNTs were sonicated for 5 min and the DMAP stabilised palladium nanoparticle dispersion was added. The composite was kept in solution through periodic sonication before being allowed to fully precipitate. As above, a detailed description of this process can be found in Ref. [27]. An aliquot of the resulting MWCNT/Pd-DMAP



Reagents and conditions:

A. HNO_3, 130°C, 24 hours.

B. $KMnO_4$ / $HClO_4$

C. EDAC, DMAP, 2-Mercaptoethylamine.HCL, RT, 24 hours.

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

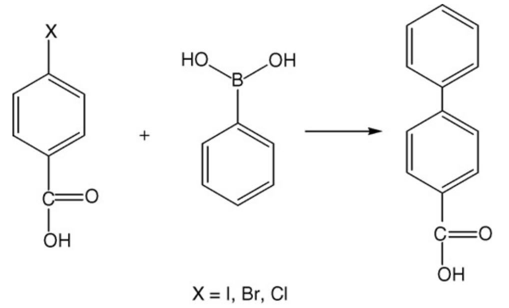


Fig. 2. Suzuki reaction of interest between phenylboronic acid and 4-halobenzoic acids.

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.

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 in the usual way.

2.2. Catalysed Suzuki reactions

The aqueous phase Suzuki reactions between phenylboronic acid and 4-iodobenzoic acid, 4-bromobenzoic acid or 4-chlorobenzoic acid (Fig. 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.

2.2.1. Suzuki reactions catalysed by DMAP stabilised Pd nanoparticle dispersions

In a typical procedure, sodium carbonate (3.0 mmol), 4-iodobenzoic acid (1.0 mmol) and phenylboronic acid (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 min. The reaction mixture was refluxed at 100 °C under nitrogen for 10 min with stirring. It was then cooled and then acidified from pH 9 to pH 1 using aqueous sulphuric acid. The product was extracted by washing with 3 × 30 mL aliquots of chloroform and subsequently the % yield was analysed using ^1H NMR. The exact same procedure was utilised for the 4-bromobenzoic acid reactions. The 4-chlorobenzoic acid reactions used the same general procedure except the reactions were refluxed for 6 h instead of 10 min and a larger amount of Pd nanoparticle dispersion (480 μL, 0.40 mol.%) was added. It is known that the rate of the Suzuki reaction is affected by the size of the halogen on the substrate [22].

2.2.2. 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-h reaction times were again used for the 4-chlorobenzoic acid reactions (with 5.8×10^{-2} mol.% Pd) while 10 min 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).

2.2.3. 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-h 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 (see above).

2.3. Yield analysis

To estimate the yield of the reactions ^1H NMR was used. All ^1H NMR spectra 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 (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 min and a subsequent ^1H NMR spectrum obtained in $CDCl_3$. The product yield was analysed 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 ^1H NMR spectra using Mestrec software.

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

3. Results and discussion

3.1. 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 h. Thus, any reactivity in the presence of the nanoparticle dispersions must be due to the catalytic activity of these dispersions.

Fig. 3 shows the % conversion of the 4-chloro-, bromo- and iodo-substituted benzoic acids to product when catalysed by various

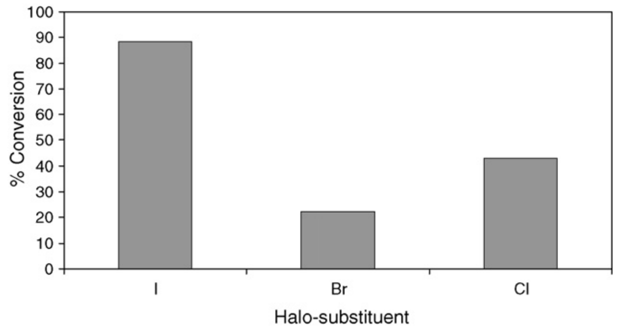


Fig. 3. Conversions of chloro-, bromo-, and iodo-substituted substrates in the Suzuki reaction promoted by Pd nanoparticle dispersions. I and Br substituted benzoic acid: 0.05 mol.% Pd and 10 min reaction, Cl substituted benzoic acid: 0.4 mol.% Pd and 6 h reaction. The nanoparticle dispersions were aged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

concentrations of the nanoparticle dispersions (see Section 2 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 h 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 1 h, 25 h, 4 days, 16 days and 25 days following preparation).

Fig. 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 h 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 h 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 h 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.

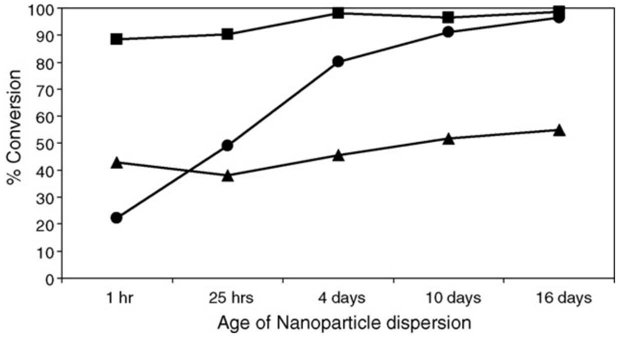


Fig. 4. Plot of % conversions of chloro- (▲), bromo- (●), and iodo- (■) substituted substrates in the Suzuki reaction promoted by Pd nanoparticle dispersions as a function of the age of the nanoparticle dispersion. I and Br substituted benzoic acid: 0.05 mol.% Pd and 10 min reaction, Cl substituted benzoic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

3.2. *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 Section 2) 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 min 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 h 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 [28–31]. 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 also, such recycling could also lead to the eventual removal of any contributions from the (soluble) 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.

3.3. *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 immobilized nano 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

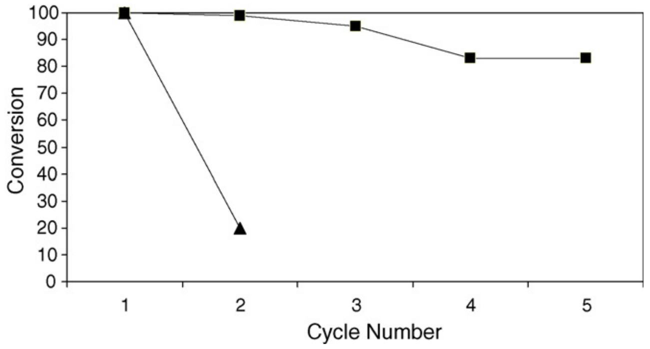


Fig. 5. Plot showing the activity of the MWCNT/Pd-DMAP NP composite catalyst (■) and MWCNT/Complex composite catalyst (▲) in promoting the reaction between 4-iodobenzoic acid and phenylboronic acid.

Section 2) 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 h 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.

Fig. 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 Fig. 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 soluble $Pd(DMAP)_4(OH)_2$ 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 another aspect of interest within this reaction mixture. TEM (shown in Fig. 6) shows that the Pd nanoparticles sinter (increasing their mean size to 7.4 ± 1.9 nm) 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. We can only conclude that this is due to a mechanism that does not involve the standard temperature-driven sintering processes.

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.

It has often been reported that the true active species in Suzuki coupling of some supported Pd catalysts are leached molecular or colloidal species [32]. We have shown that in the case of the DMAP stabilised nanoparticles a leached molecular species (the $Pd(OH)_2(DMAP)_4$ complex acted as an extremely active catalyst or catalyst precursor. In order to test whether an equivalent leaching process was operating over the composites, following the removal of the complex, we carried out an experiment to determine whether the reaction solution after the completion of a composite-catalysed reaction was itself catalytic. Such approaches have been used previously to study dissolution of several catalysts including Suzuki cross-coupling [33] and triglycerides transesterification [34].

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 six 2 h reactions. This was carried out in order to ensure that any adsorbed complex present on the initial composite was completely removed so that any catalytic species in the solution after reaction was derived from the immobilised particles.

Following this the reaction mixture was filtered while hot. An aliquot of this reaction solution was submitted for AA analysis but the levels of Pd in solution (if any) were below the detection limit of the AA spectrometer (reported at 10 ng/mL of Pd).

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 h. Following this, the mixture was again analysed for % conversion and it was found that this had increased to 31%.

This conclusively showed that following these treatments the reaction mixture itself was also catalytic and this in turn (given that reaction does not take place in the absence of catalyst – see above) proves that some catalytic species (molecular or colloid in

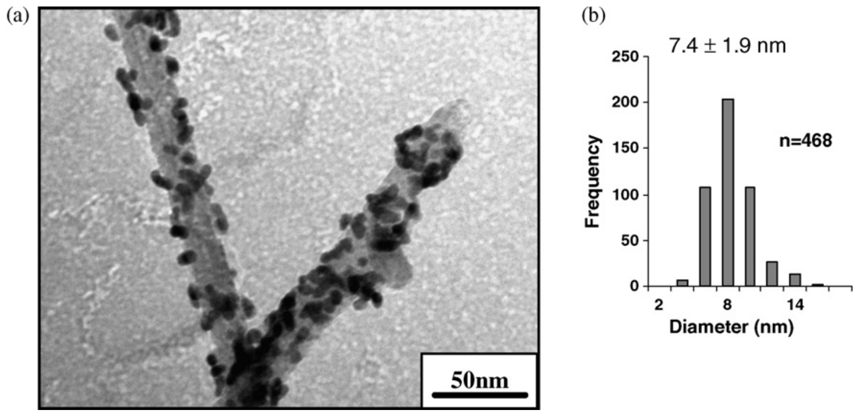


Fig. 6. (a) TEM and (b) histogram showing the average Pd nanoparticle size on the MWCNT/Pd-DMAP NP composite following catalysis of the Suzuki reaction between phenyl boronic acid and 4-iodo-benzoic acid. Note the average nanoparticle size has increased from ~3.6 ± 0.6 nm (see Fig. 1) to ~ 7.4 ± 1.9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

nature) was leached from the composite during reaction. The nature of this species (colloid or molecular in nature) unknown but its concentration must be below the detection limit of AAS.

This has shown that these nanoparticles (in common with several other supported Pd catalysts) are susceptible to leaching and that it is possible that the true catalyst involves these leached species.

4. 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 thiolated molecules chemically attached to the MWCNT surfaces.

The resultant composite is also active in the promotion of the reaction of interest although it seems that the immobilised nanoparticles can also act as reservoirs for dissolved Pd species that are also Suzuki coupling catalysts. The concentration of the latter Pd species dissolved in the reaction medium following six reaction cycles, while being sufficient to promote small amounts of conversion, is below the detection limits of AA spectroscopy.

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References

[1] M. Moreno-Manas, R. Pleixats, Acc. Chem. Res. 36 (2003) 638.
[2] J.D. Aiken III, R.G. Finke, J. Mol. Catal. A: Chem. 145 (1999) 1.
[3] A. Roucoux, J. Schulz, H. Patin, Chem. Rev. 102 (2002) 3757.
[4] M.N. Vargaftik, V.P. Zargorodnikov, I.P. Stolarov, I.I. Moiseev, D.I. Kochubey, V.A. Likholobov, A.L. Chuvilin, K.I. Zamaraev, J. Mol. Catal. 53 (1989) 315.
[5] C.-B. Hwang, Y.-S. Fu, Y.-L. Lu, S.-W. Jang, P.-T. Chou, C.R.C. Wang, S.J. Yu, J. Catal. 195 (2000) 336.
[6] F. Lu, J. Ruiz, D. Astruc, Tetrahedron Lett. 45 (2004) 9443.
[7] Y. Li, X.M. Hong, D.M. Collard, M.A. El-Sayed, Org. Lett. 2 (2000) 2385.
[8] R. Narayanan, M.A. El-Sayed, J. Am. Chem. Soc. 125 (2003) 8340.
[9] R. Narayanan, M.A. El-Sayed, J. Phys. Chem. B 105 (2001) 8938.
[10] Y. Niu, L.K. Yeung, R.M. Crooks, J. Am. Chem. Soc. 123 (2001) 6840.
[11] J.C. Garcia-Martinez, R. Lezutekong, R.M. Crooks, J. Am. Chem. Soc. 127 (2005) 5097.
[12] O.M. Wilson, M.R. Knecht, J.C. Garcia-Martinez, R.M. Crooks, J. Am. Chem. Soc. 128 (2006) 4510.
[13] S.K. Oh, Y. Niu, R.M. Crooks, Langmuir 21 (2005) 10209.
[14] Y.-S. Shon, E. Cutler, Langmuir 20 (2004) 6626.
[15] Y. Xiong, J.M. McLellan, J. Chen, Y. Yin, Z.-Y. Li, Y. Xia, J. Am. Chem Soc. 127 (2005) 17118.
[16] Y. Xiong, J. Chen, B. Wiley, Y. Xia, S. Aloni, Y. Yin, J. Am. Chem. Soc. 127 (2005) 7332.
[17] R.W.J. Scott, H. Ye, R.R. Henriquez, R.M. Crooks, Chem. Mater. 15 (2003) 3873.
[18] D.H. Turkenburg, A.A. Antipov, M.B. Thathager, G. Rothenberg, G.B. Sukhorukov, E. Eiser, Phys. Chem. Chem. Phys. 7 (2005) 2237.
[19] D.I. Gittins, F. Caruso, Angew. Chem. Int. Ed. 40 (2001) 3001.
[20] J.A. Sullivan, K.A. Flanagan, H. Mueller-Bunz, Langmuir 23 (2007) 12508.
[21] S. Paul, J.H. Clark, Green Chem. 5 (2003) 635.
[22] N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457.
[23] A. Suzuki, J. Organomet. Chem. 576 (1999) 147.
[24] Y.R. de Miguel, J. Chem. Soc. Perkin Trans. 1 (2000), 24 4213.
[25] J.A. Loch, R.H. Crabtree, Pure Appl. Chem. 73 (2001) 119.
[26] T. Sainsbury, D. Fitzmaurice, Chem. Mater. 16 (2004) 2174.
[27] J.A. Sullivan, K.A. Flanagan, H. Hain, Catal. Today 139 (2008) 154–160.
[28] A.H.M. de Vries, J.M.C.A. Mulders, J.H.M. Mommers, H.J.W. Henderickx, J.G. de Vries, Org. Lett. 5 (2003) 3285.
[29] M.T. Reetz, J.G. de Vries, Chem. Commun. (2004) 1559.
[30] W.-F. Dong, G.B. Sukhorukov, H. Mohwald, Phys. Chem. Chem. Phys. 5 (2003) 3003.
[31] K. Matos, J.A. Soderquist, J. Org. Chem. 63 (1998) 461–470.
[32] R. Narayanan and M.A. B, 109, 26, (2005), 12663–12676.
[33] R. Kranich, K. Eis, O. Geis, S. Muhle, J.W. Bats, H.G. Schmalz, Chem. Eur. J. 5 (2000) 843.
[34] M.L. Granados, M.D.A. Poves, D.M. Alonso, R. Mariscal, F.C. Galisteo, R. Moreno-Tost, J. Santamaria, J.L.G. Fierro, Appl. Catal. B: Environ. 73 (3–4) (2007) 317–326.