

# Colloidal Palladium Nanoparticles versus Commercial Palladium Catalysts for Suzuki Cross Coupling Reactions – The Influence of Surface Functionalization

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## ABSTRACT

The effect of nanoparticle (NP) surface chemistry and functionalization on the catalytic performance in Suzuki coupling is assessed. Capping ligands commonly used in colloidal synthesis such as oleylamine, dodecanethiol, propylene glycol and PVP are compared with commercial Pd on carbon. The catalysts are analyzed pre- and post-reaction with transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Capping ligands are found to have a positive or negative effect on the catalytic performance depending on the chemistry of the functional group. Capping ligands further impact on the reusability of the catalyst. Changes in the NP surface chemistry and morphology during the reaction are key deactivation pathways for catalysts, even a room temperature. In particular PVP, was observed to give excellent stability to colloidal catalysts preventing significant NP aggregation and facilitating excellent reusability.

**Keywords:** palladium, nanoparticles, capping ligands, surface chemistry, Suzuki

## 1 INTRODUCTION

The benefits of colloidal nanoparticles (NPs) in catalytic applications include the ability to tune the particle size, shape and surface chemistry. This versatility is not only advantageous for optimising catalyst design but also in understanding structure-property relationships in catalytic systems. The Suzuki-Miyaura reaction is a highly utilized reaction for aryl-aryl bond formation in organic synthesis and represents a key reaction used in the chemicals industry. These reactions are typically associated with homogeneous catalysis but there has been an enormous surge in the use of colloidal NPs for applications in Suzuki coupling reactions.[1-2] Colloidal NP catalysts can boast impressive turn over frequencies ( $10^5$ ), and recyclability of colloidal catalysts over multiple reaction cycles catalyst have also been demonstrated.[3] Recently, we have shown that the Suzuki reaction to be highly sensitive to the size[4] and shape[5] of the Pd catalyst. Furthermore, we found the mechanism for this activity stems, in part, from the leaching susceptibility of surface atoms.[6] Mechanistic studies identify leaching processes to occur in many NP catalyzed reactions.[7-9] While leaching of soluble Pd species has been shown to catalyze the Suzuki reaction it can also lead to aggregation and deactivation

of the catalyst, limiting recyclability and resulting in possible metal contamination of the reaction product. Therefore, the chemical nature of the surface can have a marked impact on the catalytic activity, stability and reusability. In this study we compare the catalytic activity of colloidal NPs capped by common stabilizing ligands typically used in colloidal synthesis with commercial Pd on carbon catalysts.

## 2 EXPERIMENTAL

Polyvinylpyrrolidone (PVP)[10], dodecanethiol (DDT)[11], oleylamine (OAm)[4] and propylene glycol (PG)[12] stabilized Pd NPs were prepared by methods previously described. Pd NPs were deposited onto activated carbon by stirring solutions overnight. The catalysts were collected by filtration and washed thoroughly with water for PVP, PG NPs and toluene for DDT and OAm catalysts. Commercial Pd/C was purchased from Sigma-Aldrich. The catalytic performance of the colloidal catalysts was compared in the cross coupling of 4-methoxybromobenzene or 4-methoxyiodobenzene (2 mmol) and phenylboronic (2.2 mmol) in EtOH/H<sub>2</sub>O (3:1), with 2 equivalents of potassium carbonate as base. Reaction profiles were monitored by gas chromatography. Products were identified against authenticated standards and quantified by calibration to obtain response factors against the known internal standard. X-ray Photoelectron Spectroscopy (XPS) was acquired using a KRATOS AXIS 165 monochromatized X-ray photoelectron spectrometer equipped with an Al K $\alpha$  (h $\nu$  = 1486.6 eV) X-ray source. Spectra were collected at a take-off angle of 90° and all spectra were reference to the C 1s peak at 284.6 eV. Transmission electron microscopy (TEM) analysis was performed using a Jeol 2100 electron microscope at an operating voltage of 200 kV.

## RESULTS

Figure 1 shows representative TEM images of the prepared NPs before and after deposition onto the catalyst support. Figure 1 (a) shows OAm capped and DDT capped NPs before immobilisation onto activated carbon. Figure 1(c) and (d) show the PVP-catalysts and commercial Pd/C. The mean diameters of the PVP, OAm, PG and DDT NPs were 3.4 nm, 3.3 nm, 4.2 nm and 3.1 nm, respectively. Commercial Pd/C is typically characterized by a broad range of NP diameters including small (< 5 nm), well dispersed NPs such as those shown in Figure 1 (d) and larger (>100 nm) metal aggregates, as shown in Figure 1 (d) inset.

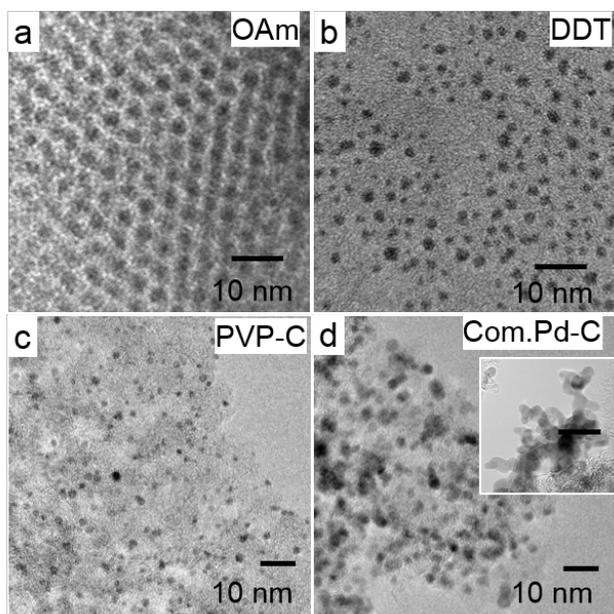


Figure 1. TEM images of unsupported (a) OAm and (b) DDT capped Pd NPs. Carbon supported (c) PVP capped NPs and (d) typical commercial Pd/C.

The catalytic performance of the colloidal catalysts was compared in the cross coupling of 4-methoxybromobenzene (**1**) and phenylboronic (**2**) in EtOH/H<sub>2</sub>O, as illustrated in the reaction scheme shown in Figure 2 inset. Figure 2 compares the reaction rate profiles for the various colloidal catalysts, using a Pd concentration of 0.5 mol % in the cross coupling for aryl bromides. All the catalysts turn over the reaction to completion at room temperature, yet there are considerable differences in the rates for each catalyst. From Figure 2, it can be seen that the reactivity trend follows PVP > OAm > PG > commercial Pd/C ~ DDT. For PVP and OAm catalysts, the initial reaction is fast as indicated by the steep reaction profile, with no induction period observed at the start of the reaction. After 45 min the reaction catalyzed by PVP-NPs is 71%, while in contrast the DDT NPs displayed a much slower conversion. A 45 min induction period was observed for the DDT catalysts before any product was formed. The large difference in activity between the thiol capped and amine capped NPs is likely due to the strongly binding thiol functional groups at the NP surface, which block access of the reagents. Furthermore, the straight chain alkyl groups exhibit a high packing density compared to the other stabilizing ligands. The PG catalysts had a similar initial reaction rate as PVP and OAm NPs, however the reaction slowed as it progressed. The smaller size of the PG ligands (C<sub>3</sub>H<sub>8</sub>O<sub>2</sub>) can less effectively stabilize Pd NPs compared to the long chain OAm and bulky PVP polymer ligands. The catalytic activity of colloidal catalysts were generally superior to commercial carbon. It is worth noting that the reproducibility of commercial Pd on carbon also varied due to variations in NP dispersion.

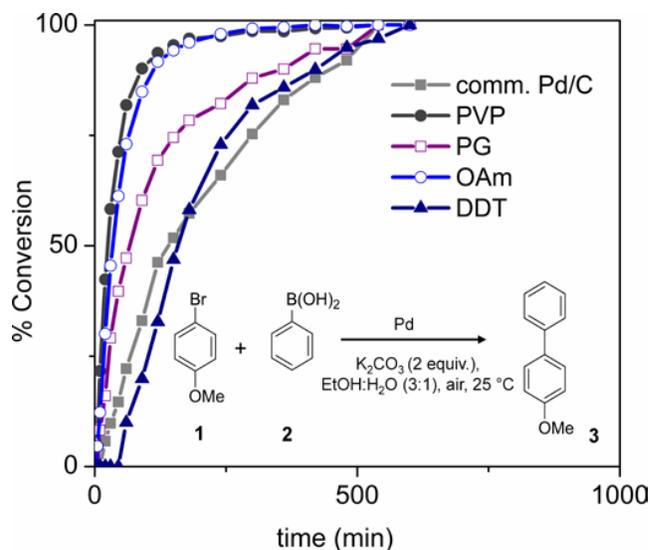


Figure 2. Reaction profile of colloidal and commercial catalysts comparing catalytic performance in Suzuki cross coupling reactions carried out at room temperature.

XPS analysis of the catalysts were carried out to evaluate the surface chemistry of the Pd NPs. Figure 3 displays the Pd 3d core level of PG-capped NP and commercial Pd/C. Both spectra show a doublet at binding energies of 335.5 eV and 341 eV, which can be assigned to Pd 3d<sub>5/2</sub> and Pd 3d<sub>3/2</sub>, respectively. Metallic Pd(0) is indicated by the peak at a binding energy of 335.5 eV. *In situ* XPS measurements of Pd determined that peaks shifted to binding energies greater than +1.5 eV surface oxide can be assigned to bulk oxide phases, while smaller shifts are attributed to surface oxide and sub-surface oxide species.[13-14] For the PG catalysts, the NPs are metallic Pd with smaller amounts of surface and bulk oxide at a binding energy of 336.3 eV and 337.1 eV, respectively. For commercial Pd/C, a large intensity peak at a binding energy of 337.1 eV can be assigned to bulk PdO. The presence of higher Pd oxidation states are indicated by the peak at a binding energy of 339 eV, which can be assigned to PdO<sub>2</sub> or Pd(OH)<sub>4</sub>. From the XPS analysis it can be seen that colloidal NPs are primarily metallic Pd(0) and commercial Pd/C is comprised mainly of PdO, due to surface oxidation. TEM analysis of the catalysis post reaction revealed that the size and morphology of the PG catalysts were well maintained during the reaction, as shown in figure 3 (c). The mean diameter and polydispersity increased slightly to 4.5 nm ± 2.2 nm. In comparison the commercial catalysts underwent significant aggregation with large diameter particles (>10 nm) readily observed by TEM analysis, as shown in Figure 3 (b). It is interesting to note that reduction of commercial Pd/C under a flow of H<sub>2</sub> gas before the reaction lowers the activity of the catalyst. This can be attributed to the reduction of the oxide to metallic Pd. For commercial Pd/C the large portion of surface oxide can be readily dissolved during the reaction. The effectiveness of commercial Pd/C stems from its pseudo-homogeneous nature with an easily leachable source of Pd. The oxide is more easily leached before H<sub>2</sub> reduction compared to leaching of metallic Pd(0).

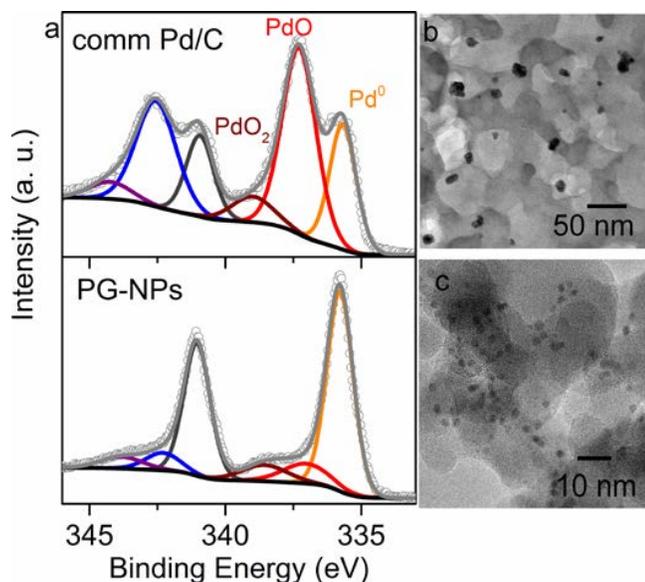


Figure 3. (a) Pd 3d core level XPS spectra of PG and commercial Pd/C. (b) TEM image of commercial Pd/C and (c) PG-catalysts after Suzuki coupling reaction.

To investigate how removing the capping ligand effects catalytic performance, OAm ligands were removed by refluxing in acetic acid.[15] XPS analysis confirmed the removal of the ligands by the absence of the N 1s peak in the survey spectra. Evaluation of catalytic performance in the Suzuki coupling reaction found that ligand removal was beneficial to catalytic activity, with the reaction going to completion faster than the capped catalysts. After 45 min the surface cleaned catalyst displayed a yield of 82% compared to a yield of 71% with the ligands present. This increase in yield can be attributed to the more exposed NP surface available for reaction when the ligands are removed. While a modest increase in catalytic performance was observed after surface cleaning, the impact on recyclability was more pronounced. The OAm capped NPs demonstrated good reusability with 8% drop in yield in the second cycle, under the same reaction conditions. A 100% yield could still be achieved by increasing the reaction time by 60 min. In contrast a significant loss in catalytic performance was observed for the uncapped NPs with a final yield of only 56%, under the same conditions. Increasing the reaction time by a further 60 min resulted in a final yield of 63%. This observation demonstrates the positive effect of capping ligands on stabilizing the Pd during the reaction leading to improved catalytic performance on recycling the catalyst.

XPS analysis was conducted to further investigate the effect of surface chemistry and cleaning in the OAm capped catalysts. Figure 4 compares the Pd 3d XPS core levels for OAm capped NPs before and after acetic acid treatment and show the NPs undergo changes to their surface chemistry as a result of the surface cleaning treatment. The as synthesized Pd NPs are mainly metallic Pd(0) as indicated by the peak at 335.5 eV. A second peak at a binding energy of 336.3 eV is attributed to

surface oxide and a smaller shoulder peak at 337.9 eV indicates the presence of bulk PdO. Analysis of the Pd 3d core level

(Figure 4(b)) after surface cleaning show an increase in surface oxidation as indicated by the greater intensity of the Pd(II) peak. The absence of capping ligands and surface oxidation of the NPs leads to greater leaching and loss of Pd during the reaction. While the leached Pd contributes to the catalyzing the reaction, it concurrently leads to catalyst deactivation, therefore significantly lowering the activity of the recycled catalyst.

The reusability of the catalysts was found to follow the trend PVP > OAm > PG > DDT > commercial Pd/C. PVP capped NPs, displayed excellent activity and recyclability with quantitative conversion being maintained over three consecutive cycles, although a longer reaction time was needed to achieve 100% yield. Lower yields on the second cycle were observed for PG and DDT catalysts, of 82% and 75%, respectively. Increasing the reaction temperature to 50 °C increases the activity of the reused and 100% yield can be achieved at evaluated reaction temperatures. To further investigate the excellent recyclability of PVP-capped catalysts changes to the NP surface chemistry and morphology were evaluated by comparing XPS and TEM of the catalyst before and after the reaction. Figure 5(a) shows the Pd 3d core level of carbon supported PVP catalyst before and after reaction. The NPs are primarily metallic with a shoulder peak attributed to some surface oxide that forms after immobilisation onto activated carbon. The surface chemistry of the NPs is also largely preserved during the reaction with no significant changes the oxidation state. A slight increase in the peak intensity ratio of Pd(0):Pd(II) is observed for the used catalyst. This can be attributed to the dissolution of the surface oxide during the reaction.[5] Analysis of the N 1s core level after the reaction displayed in Figure 5(c), show the presence of a peak at a binding energy of 400 eV, which is characteristic of the prolidone N group.[16] XPS confirms the presence of the PVP capping ligands remaining intact on the surface during the reaction. TEM of the catalyst post reaction shown in Figure 5 (b), reveal that the morphology and size distribution of the NPs is essentially preserved during the reaction.

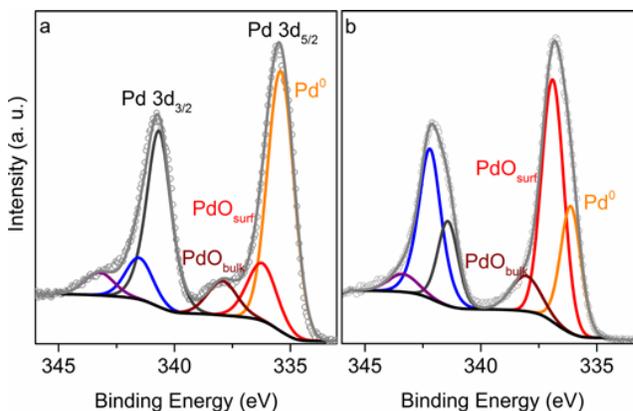


Figure 4. Pd 3d XPS core level of OAm catalysts (a) before and (b) after ligand removing with acetic acid.

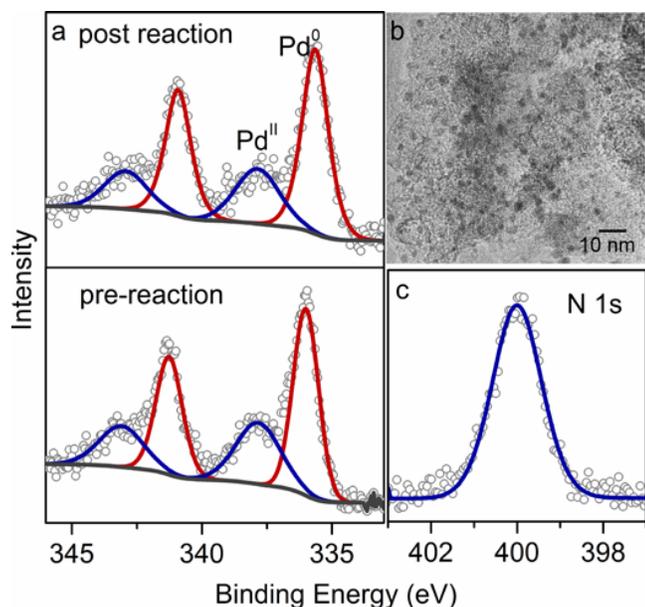


Figure 5. (a) Pd 3d XPS core level of PVP-capped catalysts before and after Suzuki coupling reaction. (b) TEM image of catalyst after the reaction and (d) N1s spectra of catalyst after the reaction.

## CONCLUSIONS

The influence of surface functionalization on the activity and recyclability of Pd NPs in Suzuki coupling reaction is evaluated. Capping ligands are beneficial to catalytic activity by stabilizing the NP during the reaction, limiting the degree of metal leaching and aggregation. The presence of capping ligands, in particular PVP, was observed to give excellent stability to colloidal catalysts preventing significant NP aggregation and facilitating excellent reusability. The work highlights the potential of modifying the surface chemistry of colloidal NPs and commercial catalysts to improve the recyclability of NPs during the reaction. Overall, a complex interplay between surface chemistry and stability under the reaction conditions influence catalytic performance and recyclability.

## REFERENCES

1. Scheuermann, G. M.; Rumi, L.; Steurer, P.; Bannwarth, W.; Muelhaupt, R., *J. Am. Chem. Soc.* **2009**, *131*, 8262-8270.
2. Balanta, A.; Godard, C.; Claver, C., *Chem. Soc. Rev.* **2011**, *40*, 4973-4985.
3. Santra, S.; Hota, P. K.; Bhattacharyya, R.; Bera, P.; Ghosh, P.; Mandal, S. K., *ACS Cat.* **2013**, *3*, 2776-2789.
4. Collins, G.; Blomker, M.; Osaik, M.; Holmes, J. D.; Bredol, M.; O'Dwyer, C., *Chem. Mater.* **2013**, *25*, 4312-4320.
5. Collins, G.; Schmidt, M.; O'Dwyer, C.; Holmes, J. D.; McGlacken, G. P., *Angew. Chem. Int. Ed.* **2014**, *53*, 4142-4145.

6. Collins, G.; Schmidt, M.; O'Dwyer, C.; McGlacken, G.; Holmes, J. D., *ACS Catalysis* **2014**, *4*, 3105-3111.
7. Pachon, L. D.; Rothenberg, G., *Appl. Organometal. Chem.* **2008**, *22*, 288-299.
8. Niu, Z.; Peng, Q.; Zhuang, Z.; He, W.; Li, Y., *Chem. Eur. J.* **2012**, *18*, 9813-9817.
9. Gaikwad, A. V.; Holuigue, A.; Thathagar, M. B.; ten Elshof, J. E.; Rothenberg, G., *Chem. Eur. J.* **2007**, *13*, 6908-6913.
10. Xian, J.; Hua, Q.; Jiang, Z.; Ma, Y.; Huang, W., *Langmuir* **2012**, *28*, 6736-6741.
11. Cargnello, M.; Wieder, N. L.; Canton, P.; Montini, T.; Giambastiani, G.; Benedetti, A.; Gorte, R. J.; Fornasiero, P., *Chem. Mater.* **2011**, *23*, 3961-3969.
12. Jeon, T.-Y.; Yoo, S. J.; Park, H.-Y.; Kim, S.-K.; Lim, S.; Peck, D.; Jung, D.-H.; Sung, Y.-E., *Langmuir* **2012**, *28*, 3664-3670.
13. Ketteler, G.; Ogletree, D. F.; Bluhm, H.; Liu, H. J.; Hebenstreit, E. L. D.; Salmeron, M., *J. Am. Chem. Soc.* **2005**, *127*, 18269-18273.
14. Lundgren, E.; Kresse, G.; Klein, C.; Borg, M.; Andersen, J. N.; De Santis, M.; Gauthier, Y.; Konvicka, C.; Schmid, M.; Varga, P., *Phys. Rev. Lett.* **2002**, *88*, 246103-246104.
15. Niu, Z.; Li, Y., *Chem. Mater.* **2014**, *26*, 72-83.
16. Collins, G.; Schmidt, M.; McGlacken, G. P.; O'Dwyer, C.; Holmes, J. D., *J. Phys. Chem. C* **2014**, *118*, 6522-6530.