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Comparing Thermal and Chemical Removal of Nanoparticle Stabilizing Ligands - Effect on Catalytic Activity and Stability

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Abstract

The use of stabilizers is an essential part of colloidal catalyst preparation, however their impact on catalytic behavior is challenging to elucidate. This report evaluates three commonly used nanoparticle (NP) stabilizing ligands, oleylamine (OAm), dodecanethiol (DDT) and the polymer polyvinylpyrrolidone (PVP). Stabilizing ligands are removed using thermal and chemical pre-treatments and the surface chemistry of the NPs is assessed using X-ray photoelectron spectroscopy (XPS). The method of ligand removal significantly altered the catalytic behavior of colloidal NPs, within the Suzuki cross coupling reaction, which is sensitive to the oxidation state of Pd and the chemistry of the capping ligand. Chemical treatment was effective for weakly binding OAm but less effective in completely removing DDT and PVP ligands, however catalytic activity of the NPs could be improved by partial ligand removal. Thermal pre-treatment decreased the activity of all the catalysts, even when the catalyst diameter and Pd surface chemistry was reasonably preserved. XPS analysis further revealed changes in the interfacial chemistry of the treated catalysts, such as the formation of oxidized sulfur species formed during annealing DDT-Pd NPs and conformational changes in PVP capping ligands as a result of thermal treatment.

Key words: nanoparticles, capping ligands, palladium, surface chemistry, XPS, Suzuki coupling

Introduction

Preparing catalysts by colloidal methods has advantages such as fine control over size, shape and composition. The ability to tailor colloidal systems allows the study of structure-property relationships not easily attainable through conventional preparation methods such as impregnation and precipitation. [1-3] An integral part of colloidal synthesis is the use of capping ligands or other additives to control growth and stabilize the nanoparticles (NPs). Capping ligands have a diverse chemistry, including small organic molecules, polymers, surfactants and bio-molecules,[4] thus the nature of stabilizing ligands can significantly alter the catalyst surface both physically and chemically, giving rise to a variety of electronic and steric effects at the reaction interface.[5] The negative impact of capping ligands has been associated with passivating active sites and poisoning the catalyst surface.[6] Amine capping ligands deactivated Pt catalysts for ethylene hydrogenation and led to low activity for CO oxidation.[7] Several studies demonstrated enhanced catalytic activity on removal of stabilizing ligands such as a 4-fold increase in activity for hydrogenation of acetylene after removal of PVP from Pd nanocubes.[8] PVA-capped Au NPs supported on TiO_2 were inactive towards CO oxidation but even partial removal of PVA enables highly effective oxidation of CO at ambient temperature.[9] Zhong *et. al.*[10] demonstrated the dynamic relationship between capping ligands and reactivity showing that PVP stabilized Au NPs displayed increased activity with subsequent ligand removal for hydrogenation of p-chloronitrobenzene but decreased activity with ligand removal for hydrogenation of cinnamaldehyde. The steric and poisoning effects from thiolate ligands on Pd NPs can also tune activity for selective catalytic hydrogenation and isomerization of

alkenes and dienes,[11] while exploiting non-covalent interactions of phenyl terminated Pd NPs can enhance selectivity for hydrogenation, isomerization and hydrogenolysis of allylic alcohols.[12] Notably, Medlin's group and co-workers[13] demonstrated several elegant examples utilizing stabilizing ligands to promote activity and/or selectivity via a variety of mechanisms including selective site blocking[14], steric effects[15] and molecular recognition.[16] Tuning catalytic performance using capping ligands has been demonstrated in a range of chemical reactions such as alkylamine capped PtCo NPs for selective hydrogenation of alkynes[17] and α,β-unsaturated aldehydes[18], thiol-stabilized Pt NPs for hydrogenation of nitroarenes[19], L-proline stabilized Pt NPs[20] for enhanced activity and selectivity towards alcohol oxidation and PVP-stabilized noble metal NPs for enhanced aerobic oxidation of alcohols.[21-23]

Catalyst recyclability and stability is also an important aspect, particularly in relation to noble metal catalysts where improving catalyst lifetime or recyclability, even at the expense of lowering activity, is often desirable. Encapsulation of NPs by stabilizing ligands has potential to impart resistance against NP aggregation and metal dissolution. Ligand stabilized NPs can also be used without the need for a support material.[24] PVA capping ligands on Au NPs lowered the activity of Au/TiO_2 catalysts but increased the stability of the catalyst upon recycling, considerably prolonging the catalyst life.[25] Pd NPs treated with C_2H_2 creates a surface coating of polyacetylene, which not only enhanced the catalytic activity for hydrophobic substrates but stabilized Pd NPs against sintering or aggregation.[26]

The Suzuki cross coupling reaction is a well-studied reaction to evaluate the catalytic activity of Pd colloidal NPs.[27-28] While the Suzuki reaction can be carried out using homogeneous catalysts, difficulty in recovering the catalyst and contamination of the final product with Pd are key drawbacks, particularly important for the synthesis of pharmaceutical molecules where the tolerated concentration of residual metal is very low (< 5 ppm). [29] While the mechanism of NP catalyzed Suzuki coupling is still debated there is a growing convergence that the

reaction is best described as quasi-heterogeneous in nature, with several studies demonstrating the critical role of Pd dissolution in the reaction.[28] The quasi-heterogeneous mechanism of NP catalyzed Suzuki reaction is likely to be sensitive to the local chemical environment of the NP, however the impact of stabilizing ligands is often not considered, with potential to influence the catalytic performance and recyclability. Surface oxide is known to influence the catalytic activity as PdO can serve as a source of soluble Pd and so evaluation of the Pd oxidation state with ligand removal is important in gaining insight into the optimal surface chemistry for NP catalyzed Suzuki reaction.

Removal of colloidal stabilizing ligands without compromising the size, morphology or oxidation state of the metal can be challenging. Several procedures for ligand removal have been developed based on thermal, UV-ozone and chemical cleaning methods.[9, 30-33] The method of ligand removal, its efficacy and the impact on the catalyst surface chemistry are all critical in determining the reactivity of NPs. Polymeric ligands such as polyvinylpyrrolidone (PVP) and polyvinyl alcohol (PVA) are particularly problematic as high temperatures (> 250 °C) are required to decompose the ligands. Thermal procedures can be suitable for NPs stabilized with small organic molecules. Low temperature thermal annealing (~185°C)[34] and rapid thermal annealing[35] in air was found to be effective for removal of ligands on noble metal NPs without altering particle size or morphology. Chemical pre-treatments such as solvent extraction, solution-based oxidizing agents and ligand displacement are beneficial methods to remove capping ligands as the treatment can be more selective towards particular stabilizing ligands.[1, 30] Solvent washing is most suited to weakly binding species and typically results in incomplete ligand removal.[9] Oxidizing treatments such as *t*-butyl hydroperoxide can remove strongly bound ligands such as triphenylphosphine from Au clusters but also induced changes in size and morphology.[36] Ligand exchange agents such as poly(acrylic acid) and poly(allylamine) polyelectrolytes[37] and nitrosonium tetrafluroborate[38] are applicable to a range

of capping ligands. Sodium borohydride acts as a chemical detergent, originally developed for cleaning planar Au surfaces but has also be shown to be highly effective for ligand removal on Au NPs.[39]

This reports investigates how the ligand removal method can influence the surface chemistry and catalytic activity of Pd NPs stabilized by dodecanethiol (DDT), oleylamine (OAm) and PVP. The catalysts are subject to thermal oxidative and chemical pre-treatments to remove the stabilizing ligands. XPS analysis assesses the effectiveness of each method and how different pre-treatments influence the catalyst surface chemistry. Chemical and low temperature thermal preserved the NP diameter and Pd oxidation state reasonability well, expect for an increase in surface oxide. The method of ligand removal can induce changes in the nature of the capping ligands such as the formation of oxidized ligand species and altered ligand conformation. The activity of the ligand stabilized and pre-treated NPs were assessed in Suzuki coupling reaction. In general, chemical treatment was least effective in complete ligand removal but increased the activity of all the catalysts while thermal treatment decreased the activity. All ligand stabilized NPs displayed superior recyclability performance compared to thermally or chemically treated catalysts.

Experimental

NP Synthesis*:* All chemical reagents were purchased from Sigma-Aldrich and used as received. DDT capped NPs were prepared using a method previously described[40]. Briefly, 20 mg K_2PdCl_4 was dissolved in H_2O/THF (1:5 v/v) followed by 250 μL of H_3PO_4 and 3.9 μL of DDT and left to stir for 5 min. A freshly prepared aqueous solution containing 23.2 mg $NaBH_4$ in 1 ml of water was added under vigorous stirring. The NPs were left to stir for 5 min. The THF was evaporated under vacuum and the NPs were redispersed in a minimum amount of hexane followed by precipitation in EtOH. The NPs were briefly sonicated and collected by

centrifugation. This purification procedure was repeated twice and the NPs were finally re-dispersed in hexane. OAm-capped NPs were synthesized following a previously reported method.[41] Briefly, 75 mg of $Pd(acac)_2$ was dissolved in 15 ml of OAm and heated to 60 °C under magnetic stirring in a N_2 atmosphere. 1 ml of triphenylphosphine was injected into the solution. In a separate flask, 300 mg of borane *t*-butylamine was dissolved in ~3 ml OA under N_2 and then injected into the Pd precursor solution and heated to 90 °C. The reaction was aged for 3 h and the NPs were precipitated by EtOH and collected by centrifuge. The NPs were subject to the same purification produce as outlined for the DDT-stabilized NPs. This purification procedure was repeated three times and the purified NPs were redispersed in hexane. PVP capped NPs were prepared using a method previously described[42]. Briefly, a 2 mM H_2PdCl_4 solution was prepared by dissolving 106.4 mg of $PdCl_2$ (0.6 mmol), 6.0 mL of 0.2 M HCl, and 294 mL of DI water. 15 ml of the 2 mM H_2PdCl_4 and 25.5 mg of PVP were dissolved in 10.5 ml EtOH and 24.5 ml water. The solution was refluxed for 3 h under air and left to cool to room temperature. *NP immobilization*: The colloidal NPs were supported on activated carbon by dropwise addition of the NP solution to the activated carbon dispersed in the same solvent. The mixtures were left to stir overnight and filtered, leaving a colourless filtrate and the supported NPs were dried in air.

Catalyst Pre-treatment: *Thermal oxidative treatment.* OAm capped catalysts were annealed at 190 °C for 5 h. DDT capped NPs were annealed at 250 °C for 5 h and PVP capped catalyst were annealed at 250 °C, 350 °C or 450 °C for 6 h. *Chemical pre-treatments:* OAm ligands were removed by refluxing in neat acetic acid (AcOH) for 12 h. The catalysts were thoroughly rinsed with water. DDT ligands were removed by stirring in 0.5 M sodium borohydride ($NaBH_4$) solutions for 5 min.[39] The catalyst were collected by centrifuge, washed with water, sonicated briefly and collected again by centrifuge. This sequence was repeated three times. PVP capped NPs were stirred in neat t-butylamine for 72 h.[43] After the cleaning treatments the

catalysts were collected by centrifuge and thoroughly washed with DI water and dried under vacuum.

Catalytic Evaluation: The catalytic performance of the colloidal catalysts was compared in the cross coupling of 4-methoxybromobenzene (2 mmol) and phenylboronic (2.2 mmol) in EtOH/H_2O (3:1), with 2 equivalents of potassium carbonate as base. Reactions were carried out in air at ambient temperature (~20 °C) using a catalyst concentration of 0.5 mol% Pd. Reaction profiles were monitored by gas chromatography using an Agilent 7890A GC system, equipped with a flame ionization detector (FID). Products were identified against authenticated standards and quantified by calibration to obtain response factors against the known internal standard. For the recyclability studies, the catalyst was recovered by centrifugation, washed in ethanol and water and re-weighed. The amount of starting reagents was adjusted in the subsequent reaction cycle to account for any loss of catalyst during recovery. Calculation of turn over frequencies (TOFs) were based on moles of Pd and the surface normalized TOF were based on the percentage of surface atoms estimated assuming a spherical morphology and the mean diameter determined by TEM analysis.[44]

Materials Characterization: X-ray Photoelectron Spectroscopy (XPS) was acquired using a KRATOS AXIS 165 monochromatized X-ray photoelectron spectrometer equipped with an Al Kα (hv = 1486.6 eV) X-ray source. Spectra were collected at a take-off angle of 90° and all spectra were referenced to the C 1s peak at 284.6 eV. Pd 3d core levels were fit with a Shirlely backgrounds and Gaussian-Lorentzian profiles. To achieve best fit, the peak positions were allowed to float with a variable fwhm ranging from 1-1.5 for metallic Pd(0) and 1.2-1.7 for oxidized Pd components. Peaks shifted to B. E. greater than +1.5 eV of the elemental Pd(0) peak are assigned to bulk oxide phases PdO, while smaller B. E. shifts are attributed to surface oxide and sub-surface oxide species PdO_{surf}[45-46]. The S 2p components are fit to a doublet with a branching ratio of 0.5 and spin-orbit splitting of 1.2 eV. Surface bound thiolate species were

fixed at a binding energy of 162.7 eV. To fit other sulfur environments, the peaks were allowed to float within the range of 163-166 eV for physisorbed, thiols, while peaks at binding energies >166 eV were assigned to oxidized sulfur species. Transmission electron microscopy (TEM) analysis was performed using a JEOL 2100 electron microscope at an operating voltage of 200 kV. Scanning transmission electron microscopy (STEM) was performed on a FEI Titian transmission electron microscope at an operating voltage of 300 kV.

Results and Discussion

To minimize size effects on catalytic activity, NPs of the same diameter (*ca* 3 nm) were synthesized with OAm, DDT and PVP as capping ligands. Figure S1 shows TEM images of the synthesized NPs. Figure 1 shows STEM images of the NPs dispersed on activated carbon and corresponding size distribution histograms for OAm, PVP and DDT stabilized Pd NPs have mean diameters and standard deviation (σ) of 3.4 nm (σ = 0.6), 3.1 nm (σ = 0.9) and 3.2 nm (σ = 0.8), respectively.

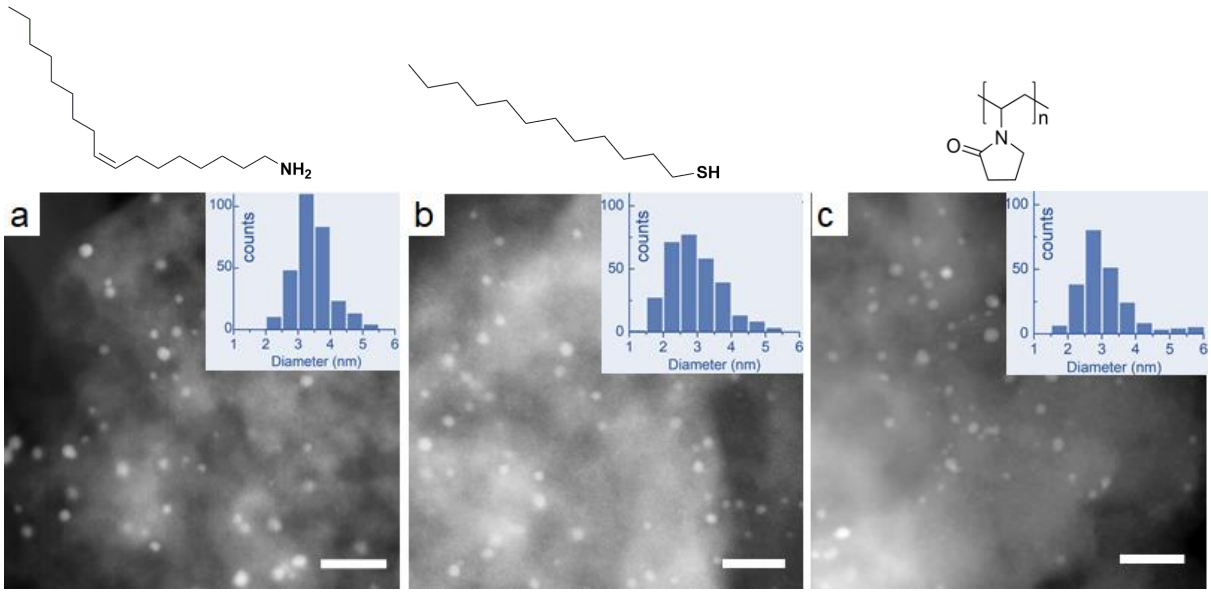


Figure 1: STEM images and corresponding diameter size distribution profile of Pd NPs stabilized with (a) oleylamine (OAm) (b), dodecanethiol (DDT) and (c) polyvinylpyrrolidone (PVP).

The Suzuki cross coupling reaction is a well-studied reaction to evaluate the catalytic activity of Pd colloidal NPs,[27-28] however the impact of stabilizing ligands used in the NP synthesis is often not considered. The reaction profiles of the colloidal NPs were first assessed to evaluate the comparative catalytic activity of different stabilizing ligands on the Pd NPs and commercial Pd/C was also assessed as a reference catalyst. TEM and STEM analysis of the commercial catalyst is illustrated in Figure S2. The commercial catalyst is characterized by a mixture of small diameter NPs, comparable in diameter to the those of the colloidal catalysts (~2-4 nm), in addition to larger Pd aggregates as shown in Figure S2. The catalytic performance of the colloidal catalysts was compared in the cross coupling of 4-methoxybromobenzene acid and phenylboronic in EtOH/H_2O, at room temperature and the catalyst concentration used in all samples was 0.5 mol%. Pd NPs generally display high activity in cross coupling of aryl bromides as illustrated in the reaction profiles Figure 2, with all three colloidal Pd NPs and commercial Pd/C catalyzing the reaction to completion at room temperature. There are marked differences in the reaction induction time and relative rate of conversion as evident in the reaction profiles for the first hour, shown in Figure 2 (b). PVP and OAm stabilized NPs are excellent catalysts with no induction period observed and yields determined after 1 h reaction time were 82 % and 73 %, for PVP and OAm Pd NPs, respectively. DDT-stabilized NPs displayed a considerable induction period of 45 min giving only a 10 % conversion after 1 h. The relatively long induction period observed for the DDT-Pd NPs is attributed to the strongly binding thiolate head group. Additionally, the straight chain saturated alkane thiol enables greater packing density, with the ligand density of small chain thiols on Au NPs was found to be ~6 molecules nm^{-2}.[47] Amines in comparison, have a weaker coordinating ability and OAm

contains a *cis* double bond in the middle of the alkyl chain giving the ligand a large effective surface footprint. Although PVP produces a sterically bulky passivation layer, the ligand only weakly coordinates to the NP surface through the O group in the pyrrolidone ring.[48] The commercial Pd/C catalyst displayed a 10 min induction period but the relative conversion after the induction period was similar to DDT with yields 1 h after the induction period being 24% and 26%, for DDT and commercial Pd/C catalyst, respectively.

Table 1 further compares the reaction turn over frequencies (TOF) and surface normalized TOF. It is worth noting that while TOFs are useful in comparing different catalysts, using TOFs as a measure of reaction rate is only valid if the number of active sites for the catalyst is known, which is not the case for Suzuki cross coupling due to the quasi-heterogeneous mechanism, so TOFs in Table 1 are estimated based on moles of Pd and surface normalized TOF based on percentage of surface atoms on Pd.[44]

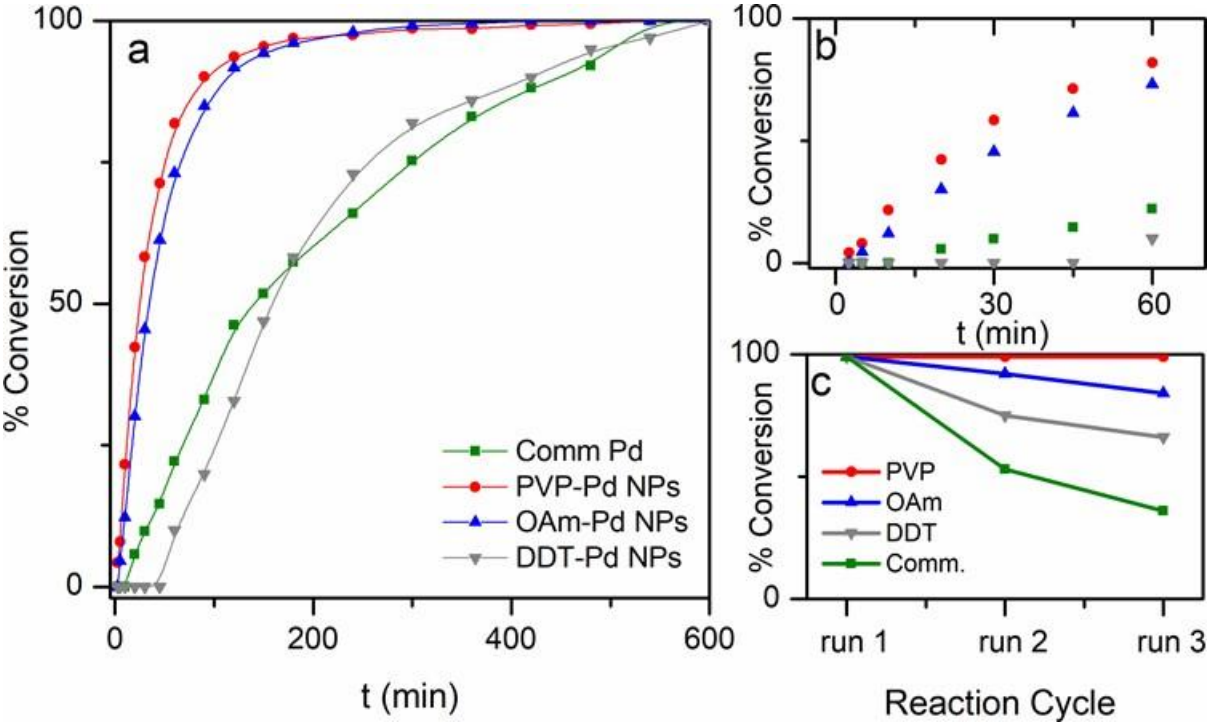


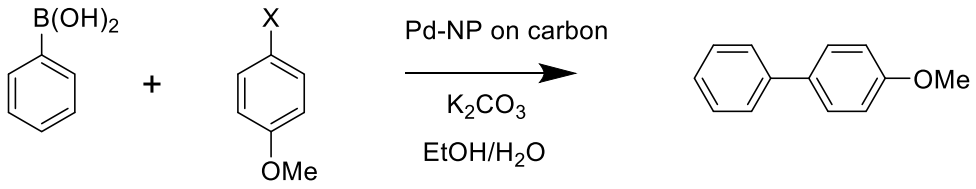
Figure 2: (a) and (b) Reaction profile of cross coupling of 4-methoxybromobenzene acid and phenylboronic in EtOH/H_2O, with Pd loading 0.5 mol%, at room temperature using carbon

supported Pd NPs stabilized by OAm, DDT, PVP and commercial Pd/C. (c) Catalytic performance of Pd catalysts over three reaction cycles.

The nature of the capping ligands also influenced the recyclability of the catalysts which is illustrated in Figure 2 (c) showing conversion over three reaction cycles. The reusability of the catalysts was found to follow the trend PVP > OAm > DDT > commercial Pd/C. PVP capped NPs, maintained quantitative conversion over three consecutive reactions. The OAm capped NPs demonstrated gradual loss in conversion over three reaction cycles and a more pronounced loss in activity was observed for the DDT-Pd catalyst. Commercial Pd catalysts displayed the poorest recyclability performance with a drop to 53% conversion on the second reaction and 36% by the third reaction cycle. The Suzuki reaction is well known to induce dissolution of Pd and XPS indicated that the commercial catalyst lost 14% mass of Pd after the reaction. [29] Metal dissolution from colloidal NPs catalyzing Suzuki coupling in aqueous solutions at room temperature is typically in the low ppm range.[3, 49]

Removal of the capping ligands was performed using thermal and chemical pre-treatment and the catalytic performance was assessed after ligand removal. Table 1 summarizes the TOFs and yields obtained before and after thermal and chemical pre-treatment demonstrating that catalytic performance is highly sensitive to the nature of the pre-treatment.

Table 1: Comparison of conversion and TOF for OAm, DDT and PVP stabilized NP before and after chemical and thermal pre-treatment.



Catalyst	% Conversion @ 1 h	% Conversion @ 6 h	TOF @ 1 h ×10^2	TOF_{surf} @ 1 h ×10^2
OAm				
No pre-treatment	73	99	146	442
Thermal	41	89	82	248
Chemical	84	99	168	509
DDT				
No pre-treatment	10	99	20	60
Thermal	trace	< 10	-	-
Chemical	44	99	88	267
PVP				
No pre-treatment	82	99	164	497
Thermal (450 °C)	< 5	22	-	-
Chemical	85	99	168	515

Reactions carried out at room temperature with 4-methoxybromobenzene (2 mmol) and phenylboronic (2.2 mmol) in EtOH/H_2O (3:1), with 2 equivalents of potassium carbonate as base and catalyst concentration of 0.5 mol% Pd. TOF estimated from % conversion after 1 h.

Oleylamine-stabilized Pd NPs

OAm is a long chain primary amine used for NPs dispersible in organic solvents. Thermal removal of OAm ligands was carried out by heating the NPs to 190 °C for 5 h.[4] Chemical removal of OAm capping ligands was performed by refluxing in acetic acid (AcOH) for 12 h.[30] XPS analysis confirmed removal of amine ligands using thermal and chemical treatment, while TEM indicated no appreciable changes to the NP size after the pre-treatments, which is consistent with literature reports for Pt catalysts.[34] Table 1 shows that OAm removed using AcOH improved catalytic activity with higher conversion of 84% after 1 h compared to 73% with the OAm ligands present. In comparison, OAm ligands removed by annealing decreased the catalytic activity with conversion at 37% after 1 h and a final conversion of 89% compared to quantitative conversion achievable for OAm stabilized and the chemically treated catalyst. The impact on recyclability is shown in Figure 3(a) and both pre-treated catalysts displayed poor recyclability performance demonstrating the positive stabilizing effect of capping ligands. The OAm stabilized NPs displayed an 8% drop in yield for the second reaction cycle compared to a 36% drop for chemically cleaned OAm and 33% reduction for thermally cleaned OAm catalysts.

In the case of OAm capped Pd NPs, chemical pre-treatment increased activity while thermal treatment deceased catalyst activity. TEM analysis indicated no appreciable changes to the NP size after either treatment, so to gain further insight into the catalytic behavior the surface chemistry of the NPs was evaluated. Pd NPs readily oxidize to decrease surface energy and it should be noted that assignments of the Pd 3d core level vary in the literature. In this study, we use those reported by Ketteler and co-workers, using *in situ* XPS measurements of Pd.[45] Peaks shifted to binding energies (B. E.) greater than +1.5 eV of the elemental Pd(0) peak are assigned to bulk oxide phases PdO, while smaller B. E. shifts are attributed to surface oxide and sub-surface oxide species PdO_{sur},[45-46] formed from passivation of Pd through dissociative chemisorption of oxygen.[8] Consequently, some in surface oxide is to expected with ligand removal. The presence of Pd oxidation states > + 2 are indicated by the peaks with a B. E. greater than 339 eV and are assigned to PdO_2 or $Pd(OH)_4$. See Experimental section for further details. Figure 3 (b) compares the Pd 3d XPS for OAm Pd NPs to the pre-treated catalysts. The OAm NPs are mainly metallic Pd as indicated by the peak at a B.E. of 335.5 eV and minor oxide contributions are observed at 336.3 eV (18%), which is attributed to surface oxide PdO_{surf} and a smaller shoulder peak at 337.9 eV (11%), assigned to bulk oxide. Both chemical and thermal treatment preserve the Pd surface chemistry reasonably well, with no bulk oxide formed but surface oxide species were formed due to passivation of Pd through dissociative chemisorption of oxygen, which can be expected due to ligand removal.[8] Chemical pre-treatment increased surface PdO (59%) at the expense of metallic Pd(0), and annealing also increased surface oxide (33%) but to a lesser degree. Thus for the case of OAm capped NPs, both pre-treatments preserved the NP diameter and induced some surface oxide formation, yet opposite effects on catalytic activity were observed. The presence of surface oxide has been shown to increase activity in Suzuki reaction as the oxide serves as a source of soluble Pd^{2+},[28] which correlates with the enhanced activity for chemically treated NPs but indicates that

additional factors contribute to the observed activity. Although N species were not detected in the OAm-Pd catalysts after annealing, the presence of adventitious hydrocarbon remaining on the NP surface cannot be ruled out, considering the relative low anneal temperature, which may account for the lower reactivity of the annealed catalysts.[50] Su and co-workers demonstrated that Pd NPs supported on carbon nanotubes (CNTs) rich in oxygen functional groups (-OH, COOH), formed after nitric acid treatment, displayed an 8-fold increase in the TOF compared to unfunctionalized CNTs. [51] Further studies reported acidic functional groups on CNTs increase activity in Suzuki coupling reactions through stronger interaction with Pd NPs, while N-doped CNTs display lower activity due to weaker Pd-N interactions.[52] Evaluation of the O 1s core level of the AcOH treated OAm catalysts, shown in Supporting Information Figure S3, reveals a considerable increase in the intensity of C=O component at 531 eV after AcOH treatment, indicative of residual AcOH species on the catalyst after chemical treatment, despite through washing with water and drying under vacuum. Although the chemical treatment preserved the NP diameter and Pd surface chemistry, the local chemical environment was altered through the introduction of acidic functional groups, which in this case may benefit catalytic activity in the Suzuki reaction.

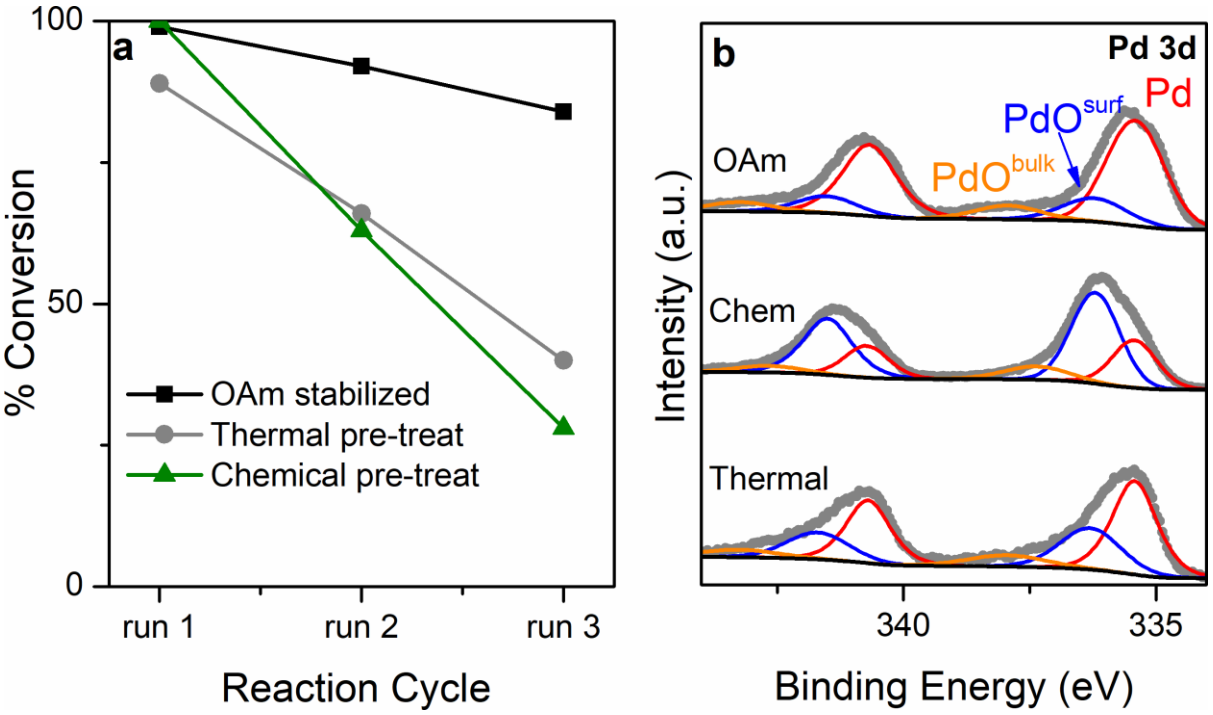


Figure 3. (a) Recyclability performance of OAm stabilized Pd NPs before and after chemical and thermal pre-treatment to remove capping ligands. (b) Pd 3d core level spectra of OAm capped Pd NPs after ligand removal by chemical and thermal pre-treatment.

Dodecanethiol Stabilized Pd NPs

Alkanethiols are one of the most commonly used capping species for metal NPs due to their excellent passivation properties. Thiols often lower catalytic activity due to strong binding with catalytic sites or poisoning effects through the formation of sulfides. A significant decrease in the catalytic activity is observed for DDT-capped Pd NPs compared to OAm or PVP, as shown in Figure 1. DDT was removed from the NPs by chemical pre-treatment using aqueous $NaBH_4$ solutions.[39] Hydride species generated from $NaBH_4$ decomposition in water displace thiol groups due to their stronger binding affinity. Chemical pre-treatment considerably enhanced activity, with a four-fold increase in conversion after 1 h, as shown in Table 1. Thermal treatment was carried out by annealing the samples at 250 °C in air for 5 h, which effectively

deactivated the catalyst towards the Suzuki reaction under the model reaction conditions. Analysis of the Pd 3d core level shown in Figure 4 revealed that chemical pre-treatment preserved the Pd surface chemistry with a minor increase in surface and bulk oxide observed, as can be expected due to removal of capping ligands. The Pd 3d core level is also shifted +0.4 eV now centred at 335.5 eV. The shift to a higher B. E. is associated with decreased electron density on the Pd after ligand removal and illustrates the electronic influence of the thiol ligands on the Pd NPs.[53]. Thermal treatment induced formation of bulk PdO with the Pd 3d doublet now centred at 337.5 eV, as shown in Figure 4(c). TEM analysis revealed some broadening in the size distribution after annealing with a mean diameter of 7.9 nm (see Supporting Information Figure S4), however this should not account for complete deactivation of the NPs as large NPs (> 20 nm) can effectively catalyse the Suzuki reaction under the same room temperature conditions and catalyst loading.[3, 54] Furthermore, PdO is well known to catalyze the Suzuki reaction and typically displays high catalytic efficiency.[28] To further elucidate the impact of surface oxidation, the catalytic activity of a reference PdO catalyst was assessed under the model reaction conditions. The rate profile shown in Figure 4(e), illustrates that PdO effectively catalyses the reaction with high conversion for 0.25 mol% and 0.5 mol% Pd loading, respectively. Conversely the PdO derived from the annealed DDT sample showed no activity and conversion remained < 20% when the catalyst loading was doubled to 1 mol% as illustrated in the reaction profile.

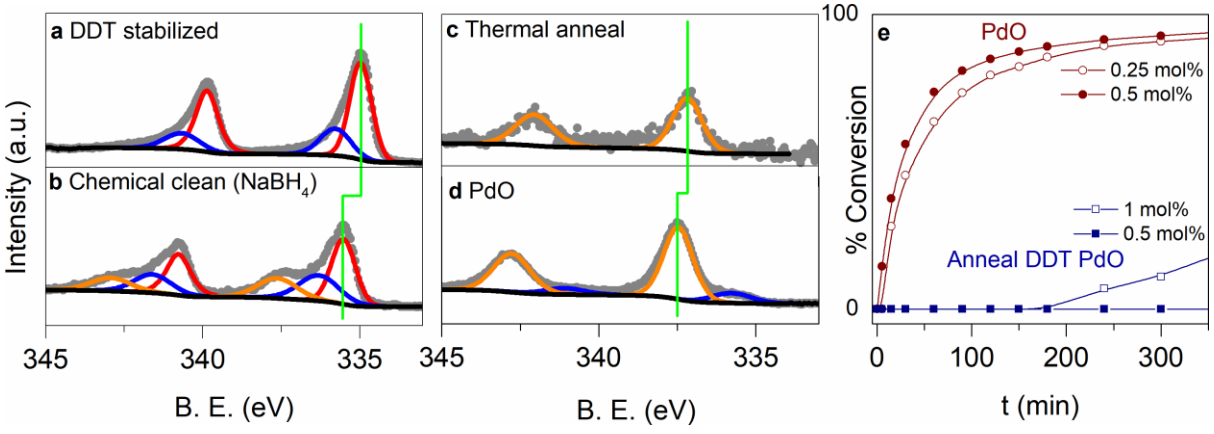


Figure 4. Pd 3d core level spectra of (a) DDT-stabilized Pd NPs (b) after thermal oxidative treatment at 280 °C and (c) after chemical cleaning treatment with aqueous $NaBH_4$ (d) commercial PdO catalyst. (e) Reaction profile comparing catalytic performance of PdO and PdO derived from annealed DDT catalyst.

Figure 5 compares the S 2p core level spectra for DDT-Pd NPs before and after thermal and chemical pre-treatment. The increased signal to noise ratio in the thermal and chemically treated catalysts is associated with the lower concentration of sulfur species due to their removal in the cleaning process. Table 2 quantifies the effectiveness of the thermal and chemical methods in removing surface bound thiolates. Analysis of the S 2p core level, displayed in Figure 5 (a) shows the DDT-stabilized Pd NPs with a doublet at a B. E. of 162.7 eV, assigned to the surface bound thiolate group.[55] A minor contribution of unbound thiol species at 164.7 eV and oxidized thiol species at 167.5 eV are also observed. It is typical to observe multiple sulfur environments on thiol passivated surfaces.[55] Figure 5(b) shows the S 2p after annealing and the absence of a peak at 162.7 eV indicates removal of surface bound thiolates. The S:Pd ratio decreased from 0.68 to 0.09, which correlates to removal of ~87% of the organic ligands. While annealing effectively removes surface bound thiolates, XPS analysis clearly identifies the presence of residual sulfur species consisting of phyisorbed (B. E. > 164 eV) and oxidized species (B. E. > 166 eV). A notable difference in the surface chemistry of the annealed catalyst is the presence of highly oxidized sulfur species at 170 eV, typically assigned to sulfonates or sulfates.[56] The formation of oxidized sulfur species formed under annealing may contribute to the poor catalytic behaviour of the annealed catalyst, as sulfur species are well known for catalyst deactivation. Figure 5(c) shows the S 2p core level after chemical pre-treatment and shows it is less effective than thermal treatment in removing bound thiolates, as the associated B. E. at 162.7 eV is still detected. Table 2 shows the S:Pd ratio decreased from 0.68 to 0.39 after chemical treatment, corresponding to ~54% of ligands removed. Furthermore,

the % of thiolate species (B.E. 162.7 eV) decreased from 72% in the DDT-Pd NPs to 41% after chemical cleaning. Importantly, while the chemical pre-treatment was less effective in removing the ligands, the chemical treated catalysts displayed superior performance compared to the thermally treated catalyst, demonstrating that partial ligand removal can effectively enhance catalytic activity.

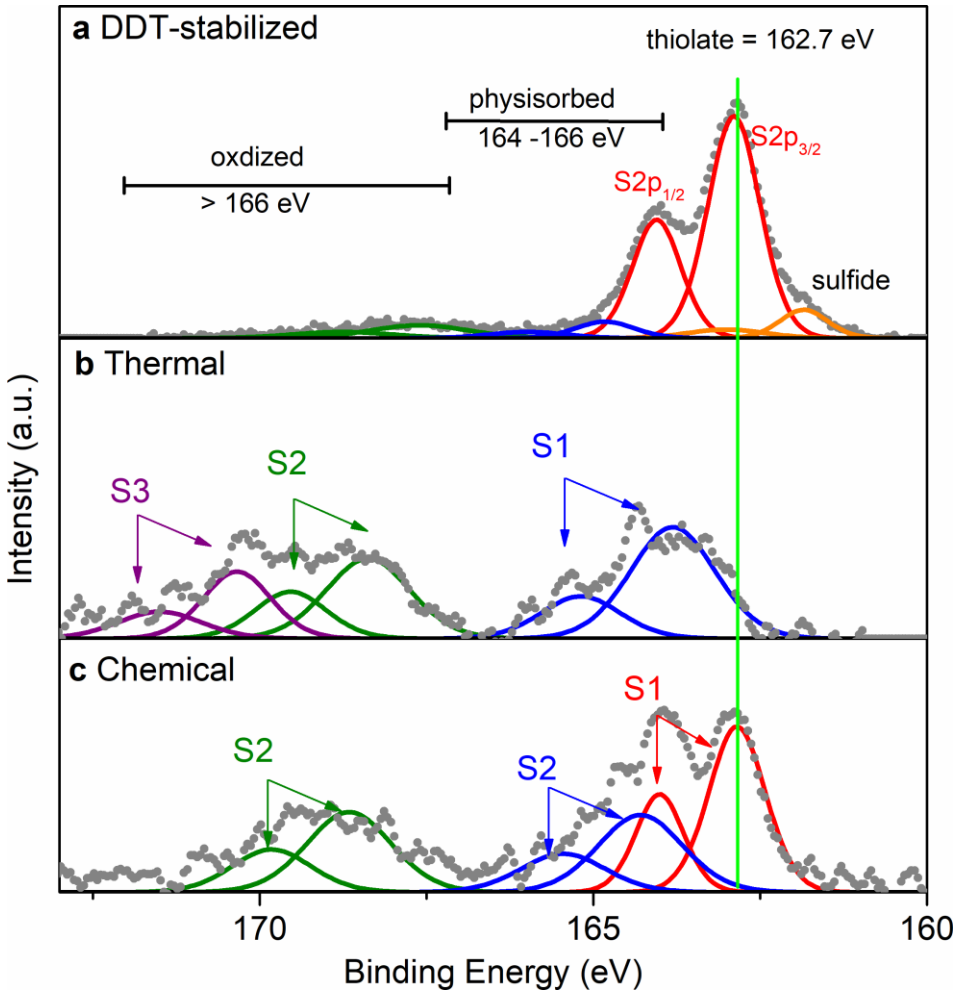


Figure 5. Background subtracted S 2p core level spectra of (a) DDT-stabilized Pd NPs (b) after thermal oxidative treatment and (c) after chemical cleaning treatment with aqueous $NaBH_4$.

Table 2: Comparison of thermal and chemical pre-treatment for DDT-Pd NPs

	DDT-Pd NPs	**Thermal treatment**	**Chemical treatment**
S:Pd	0.68	0.09	0.39
% thiolate species* (B.E. 162.7 eV)	72%	Not detected	41%

*Based on integrated area under the S 2p core level.

PVP-stabilized Pd Catalysts

The bulky, amphiphilic and non-toxic nature of PVP make it an attractive stabilizing ligand and preferential adsorption onto certain crystallographic facets, has led to wide use for shape controlled NP synthesis.[57] The large molecular weight of polymer capping ligands means high annealing temperatures are required to remove the ligands, inevitably leading to NP agglomeration. Annealing the PVP NPs at 450 °C for 5 h resulted in NP aggregation with NPs adopting an irregular morphology (Figure S5). The mean diameter increased to 9.4 nm and catalytically activity considerably decreased as shown in Table 1. Literature studies reveal that even partial removal of polymer ligands can have a considerable impact on catalytic performance,[9] so the catalysts were annealed at 250 °C, 350 °C and 450 °C. Figure 6 (a) shows the percentage of PVP removed as a function of the anneal temperature and the % conversion in the Suzuki reaction with removal of PVP from the Pd catalyst. Interestingly, a sharp drop in the conversion was observed after annealing at 250 °C, when only 18 % of the PVP is removed. Conversion remained low but did not significantly change on further annealing from 350 °C to 450 °C, after which 96 % of the PVP is removed. Figure 6(b) shows the PdO:Pd ratio derived from the peak area in the Pd 3d core level with oxidation increasing with anneal temperature. Evolution of the Pd 3d and O 1s core level with increasing anneal

temperature is shown in Figure 7(a) and 7(b), respectively. The as synthesized PVP-NPs are characterized by mainly metallic Pd and surface oxide. The O 1s spectra are somewhat obscured by overlap with the Pd $3p_{3/2}$ peak at 533 eV, so to limit further interface of O signals from the carbon support, the PVP Pd NPs were annealed as thin films prepared on Au coated Si. The O species associated with PVP occur at a B. E. of 532.7 eV and the formation of bulk PdO is clearly observed in the O 1s spectra at 350 °C with a peak appearing at ~529 eV.

In terms of correlating the surface chemistry to the catalytic performance in the Suzuki reaction, the poor catalytic activity observed at higher annealing temperatures (350 °C, 450 °C), in not unexpected and can be associated with NP aggregation (Figure S5). The poor catalytic performance of the NPs under low temperature annealing at 250 °C, is again noteworthy. At 250 °C the Pd 3d spectrum shows a partially oxidized surface (~doubles compared to the as-synthesized NPs) and partial ligand removal (18%) all of which should benefit the quasi-heterogeneous mechanism of the Suzuki reaction. Consistent with the behaviour observed for the annealed OAm and DDT catalysts, the activity decreased despite reasonable preservation of NP diameter, indicating additional factors influencing the catalytic activity.

The N 1s core level shown in Figure 7(c) illustrates changes in the N chemistry on exposure to annealing conditions. PVP capped NPs display a peak at 400 eV assigned to the amine group[48]. Thermal annealing at 250 °C results in the appearance of a secondary peak at 401 eV, associated with oxidized and protonated N species.[58] Changes in ligand conformation are important as enhanced catalytic activity of PVP stabilized NPs has been attributed to electron donation by PVP[22] and favorable interactions between PVP and reacting species.[59] Conformational changes in the PVP ligands under low temperature annealing, are also illustrated in the C 1s core level shown in Figure 7(d). To prevent interference from the carbon support, the PVP-Pd NPs were annealed as thin films on Si substrates. The C 1s core level of

the PVP-Pd NPs contains 3 carbon environments assigned to C-C (284.8 eV), C-O/C-N (285.9 eV) and C=O (287.6 eV) species. Annealing at 150 °C, gives an additional carbon environment observed at 286.5 eV, which increases in intensity with annealing temperature and is associated with oxidation of the pyrrolidone N.[48] Further annealing results in an upward shift of the C=O peak associated with imide formation.[60] Louie *et al.*[60] reported that oxidation of PVP stabilized Au NPs resulted in conformational collapse of the PVP ligands around the NP. Such changes in ligand conformation may be responsible for the sharp decrease in activity after annealing at 250 °C, when only 18% of the PVP has been removed. Conformational ligand changes giving rise to poor catalytic performance of the annealed PVP-Pd catalyst is further supported by the catalytic behaviour of chemically treated PVP-Pd NPs. Chemical pre-treatment was carried out using *t*-butylamine, which is reported to remove PVP from Pd nanocubes[43], however this treatment was much less effective for small diameter NPs, only removing ~20% of the PVP capping ligands as estimated by the N:Pd XPS ratios. The lower efficiency of the *t*-butylamine may be due to different binding modes of PVP, which is known to be size and shape dependent.[48] In contrast to the thermally treated catalyst, partial removal of PVP by chemical treatment slightly improved the catalytic activity as shown in Table 1, suggesting that the conformational changes induced by thermal treatment likely play a role in the lower activity observed for the annealed catalysts. XPS analysis further revealed that the presence of PVP on the NPs is very persistent on the Pd surface and gives rise to high stability under the reaction conditions. The Pd 3d and N 1s core level before and after the reaction, shown in Figure S6 and S7, respectively, display no change, while TEM analysis of the NPs post reaction (Figure S8) show the NP size and dispersion to be well-maintained. The PVP-Pd NPs were the only catalyst to maintain quantitative conversion on recycling over three cycles and this recyclability performance is attributed to stabilizing effect of PVP on the Pd NPs preserving the NP size, morphology and surface chemistry under the reaction conditions.

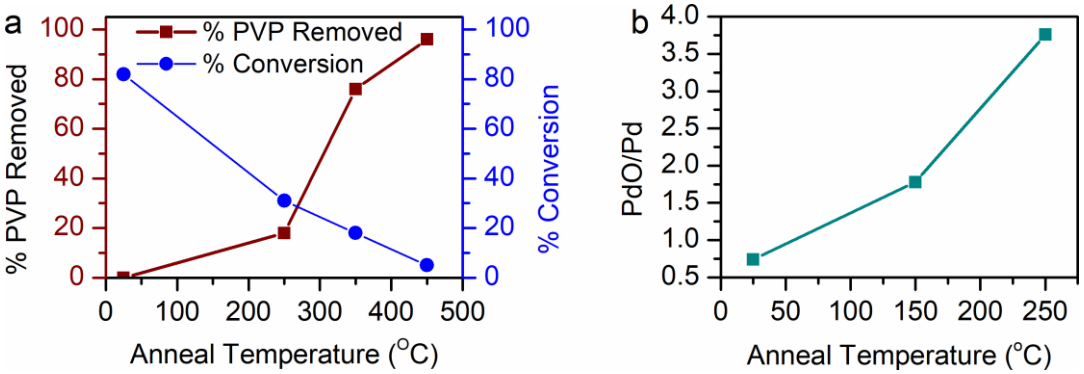


Figure 6. (a) Percentage PVP removed and % conversion obtained as a function of anneal temperature. (b) PdO:Pd peak area ratios obtained from the Pd 3d core level.

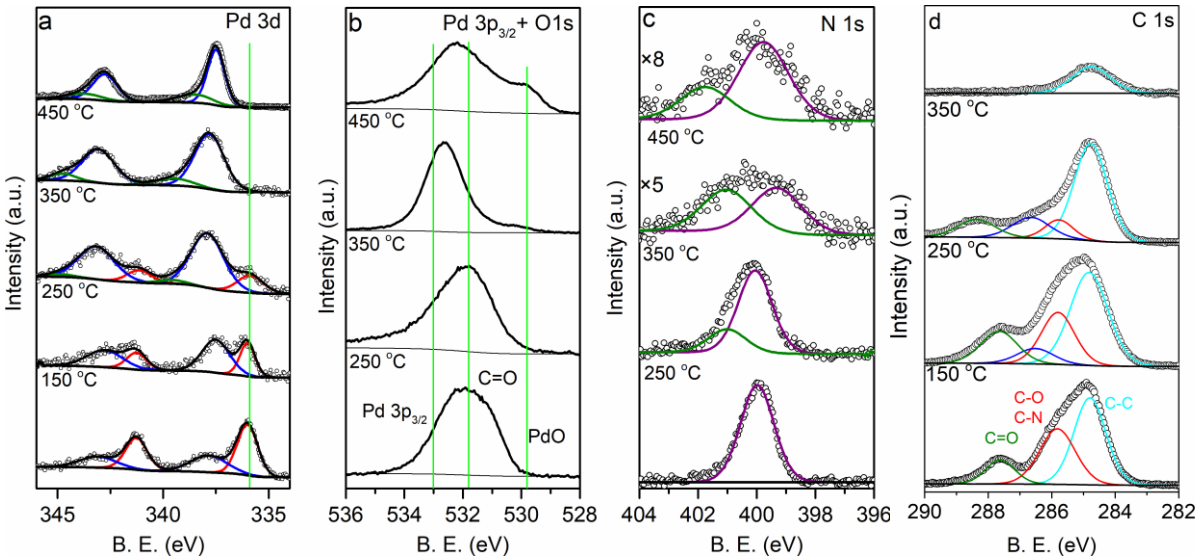


Figure 7. (a) Pd 3d (b) O1s (c) N 1s and (d) C 1s core level of PVP-capped Pd NPs under different annealing temperatures.

Conclusions

This study reveals a complex interplay between the nature of catalyst pre-treatments to remove capping ligands and the impact on catalyst activity but a number of trends can be identified. Annealing treatment was found to decrease the activity of all three colloidal catalysts, while chemical pre-treatments were found to increase activity, however the catalytic enhancement

observed in the Suzuki reaction may not be simply correlated to removal of the capping ligands without considering changes in the surface chemistry of the Pd and the ligand. Weakly binding OAm ligands could be effectively removed under low temperature annealing and by chemical methods using AcOH. Chemical pre-treatment using $NaBH_4$ was less effective for strongly binding DDT ligands, leading to incomplete ligand removal, however partial ligand removal enhanced catalytic activity. XPS analysis identified that while annealing DDT-Pd NPs completely removed surface bound thiolates, residual physisorbed and oxidized species remained on the surface, leading to decreased catalytic activity. Chemical cleaning of PVP using *t*-butylamine, lead to partial ligand removal, but again increased catalytic activity. Removal of PVP by thermal annealing required high temperatures (450 °C) leading to NP aggregation. Annealing at low temperatures preserved the NP diameter and induced conformational changes in the PVP ligands, which negatively impacted on catalytic performance.

The quasi-heterogeneous mechanism of the Suzuki reaction is known to be influenced by the presence of surface oxide, which serves as a source of soluble Pd. Increased activity observed for all the chemically treated catalysts can be attributed to the removal, or partial removal of ligands and an increase surface oxide giving rise to soluble Pd^{2+}. The decreased catalytic activity annealed samples is more complex. The despite preservation of NP diameter (except for high temperature annealing), ligand removal and increased surface oxide, which typically enhances catalytic activity, the performance of the annealed catalysts were lower than the ligand stabilized catalysts or chemically treated catalysts. XPS analysis identified the presence of residual surface species sulfur and conformational changes in ligands influence the catalytic performance. All three ligand stabilized NPs displayed greater catalyst recyclability compared to thermal and chemically treated catalysts. In particular, the interaction between Pd and PVP

contributed to the excellent stability and recyclability performance of PVP-stabilized Pd NPs in the Suzuki reaction.

Understanding the role of ligands is complex, the reactivity trends observed under the reaction conditions studied here (EtOH: H_2O solvent, room temperature reaction) may be altered by different reaction parameters such as elevated temperature or solvents. This work also demonstrates the importance of evaluating the catalyst surface of both the Pd oxidation state and organic capping ligands in the Suzuki coupling reaction, which is highly sensitive to the local chemical environment and surface oxidation effects.

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Notes

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