

Pd Nanoparticles¹

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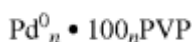
Encyclopedia of Reagents for Organic Synthesis

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DOI: 10.1002/047084289X.rm00337u.pub2

Article Online Posting Date: September 15, 2008

Abstract



[7440-05-3]

(hydrogenolysis catalyst, benzyl group removal, metal clusters, palladium, nanoparticles)

Physical Data: clear light brown solution in EtOH, EtOH–water.

Form Supplied in: aqueous ethanolic solution, powder after freeze dry, or ethanolic solution.

Preparative Methods: a 0.6 mM solution of H₂PdCl₄ containing 40% ethanol and 100 monomeric molar equivalent of PVP [poly(*N*-vinyl-2-pyrrolidone)] (average M_w = 6000–10000) was refluxed under N₂ to obtain monodispersed Pd nanoparticles, presumably with a mean diameter of ca. 17 Å, according to the method in reference 2. The H₂PdCl₄ solution was prepared from PdCl₂ and aq HCl. During the reduction, the yellow color changes to light brown where no precipitation was observed. The solvent was evaporated off to remove HCl and a large amount of water, and the resulting residue was re-dissolved in 98% EtOH (or in MeOH) for hydrogenolysis. Excess amounts of PVP further stabilize the palladium metal clusters; this is especially important if the reagent is used in the reaction with solid supported compounds. For more background research on heterogeneous catalysts in organic reactions, see references 3-6.

Handling, Storage, and Precaution: the reagent should be stored under inert atmosphere.

Original Commentary

Hydrogenolysis of Tetra-*O*-benzyl Glucopyranose

Palladium nanoparticles (2 μmol as Pd atom; 0.1 atom equivalent based on substrate)

in EtOH or MeOH (1 ml) were added to a solution of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (10.8 mg, 20 μ -mol) in EtOH or MeOH (1 ml). The resulting mixture was stirred at room temperature under an H₂ atmosphere for 2 h. The catalyst was removed by gel permeation chromatography. The reaction time was approximately ten times shorter than the conventional 10% Pd/C under the same conditions. An essentially quantitative yield was obtained for each reaction.

Hydrogenolysis of Benzyl Groups From Solid Supported Carbohydrates

2,3,4,6-Tetra-*O*-benzyl- α - and β -D-glucopyranosides supported on PEGA resin through the terephthalamide of 6-aminohexan-1-ol (30 mg) was added to a solution of palladium nanoparticles (1.5 μ -mol as Pd atom) in 3:2 water–EtOH (2.5 ml). The slurry was shaken at 40 °C under an H₂ atmosphere for 36 h. Precipitation of the catalyst inside the PEGA resin was observed. The debenzylated compounds are cleaved from the resin by saponification and the solution was neutralized. The solution was analyzed by HPLC and complete debenzylation was confirmed by co-injection of synthetic authentic samples.

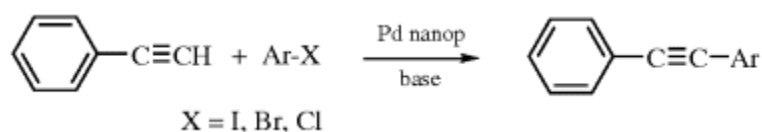
First Update

The use of metal nanoparticles in catalysis⁷⁻¹¹ (including Pd nanoparticles) is a field that has experienced significant growth in the last years. Many kinds of stabilizers, supports, and synthetic procedures have been described. Palladium(0) nanoparticles (Pd NPs) have mainly been used in hydrogenation reactions of alkenes, alkynes, arenes, and other organic substrates, in C—C bond-forming reactions (Sonogashira, Heck, Suzuki coupling) and in oxidation reactions. This update manuscript covers the literature from 2001 to May 2007 and is organized by reaction types. Bimetallic nanoparticles containing palladium as one of the metals will not be considered.

Sonogashira Reactions

The coupling between aryl halides and terminal alkynes (Scheme 1) has been performed with Pd NPs. Phenylacetylene has been used as the alkyne counterpart in most cases. Choudary¹² coupled this alkyne with activated and deactivated chloroarenes as the most challenging substrates, with a layered double hydroxide (LDH) supported nanopalladium catalyst. This copper and phosphine-free process was performed in a THF-water mixture at 80 °C, using triethylamine as base. Recycling of the LDH-Pd catalyst was successfully achieved (five cycles) in the reaction between phenylacetylene and chlorobenzene.

Scheme 1.



Park¹³ reacted phenylacetylene with a less challenging activated aryl iodide in DMF at 110 °C with Pd NPs encapsulated in a silica matrix. Triethylamine was also the base of choice, but copper iodide (4 mol%) was added in this case. The same author¹⁴ has described the same reaction under analogous conditions using Pd NPs dispersed in an organic polymer of cross-linked polystyrene. In both cases,^{13,14} recycling is not mentioned for this coupling.

Several terminal acetylenes were coupled with aryl iodides and activated aryl bromides in a copper- and ligand-free Sonogashira reaction that proceeds at ambient temperature under ultrasound irradiation, with triethylamine as base and acetone or room-temperature ionic liquid (IL) as solvents.¹⁵ Palladium chloride was used as the source of palladium(0) nanoparticles (3–8 nm in acetone, 10–20 nm in IL) formed in situ under these sonochemical conditions as shown by transmission electron microscopy (TEM) measurements. Ultrasound not only generated the nanoparticles but also enhanced the activity of the catalytic nanoparticles in the reaction. The use of IL offered the advantage of easy recycling (5 cycles) of the nanocatalyst.

Poly(vinylpyrrolidone) (PVP) stabilized palladium metal colloids¹⁶ have been described as recoverable catalyst in the Sonogashira coupling of several aryl bromides and iodides with several terminal alkynes. The metal can be recovered and recycled by addition of diethyl ether and simple decantation of precipitated Pd-PVP, eight consecutive trials being performed without significant loss of activity. The protocol involved an optimized environmentally-sound reaction system (no ligand, no copper, no amine, recoverable palladium), with potassium carbonate as base and ethanol as solvent at 80 °C.

Rothenberg¹⁷ tested the catalytic activity of embedded palladium nanoclusters in polyelectrolyte microcapsules in the coupling between phenylacetylene and 4-iodotoluene. A fast reaction was achieved (15 min) in DMF at 110 °C, using tetrabutylammonium acetate as base. The microcapsules could be easily filtered from the reaction mixture at the end of the reaction and could be reused. However, the solvent system should be optimized, as extensive leaching of the clusters into DMF and out of the shells was observed, a fact that precluded an effective recycling.

The same group tackled the question of which are the true catalytic species in palladium nanocluster-mediated Sonogashira cross coupling.¹⁸ They concluded that soluble species must be present in the system when Pd nanoclusters are used as catalysts, with two possible mechanistic pathways being suggested.¹⁹ They tested the Sonogashira reaction between phenylacetylene and iodobenzene with Pd nanoparticles generated from palladium nitrate and TOAG.

Corma and García²⁰ reported the in situ formation of Pd NPs (2–5 nm) in a copper and phosphine-free Sonogashira reaction of phenylacetylene with deactivated aryl bromides and activated aryl chlorides performed with an oxime carbapalladacycle derived from 4-hydroxyacetophenone. Poly(ethylene glycol) (PEG) and imidazolium ionic liquids were tested as solvents, and cesium acetate was the base of choice employed. PEG as the reaction medium provided higher activity, acted as a stabilizer of the nanoparticles formed in the reaction, and allowed easy recycling of the catalytic

system (5 cycles) by liquid-liquid extraction with hot diethyl ether. The same authors²¹ developed a PEG-anchored carbapalladacycle as a recyclable soluble catalyst for C—C couplings in PEG as the most convenient solvent. Although this polymer was stable upon heating in PEG, it decomposes during catalytic reactions to give less active palladium nanoparticles. In the Sonogashira couplings of activated aryl bromides, the catalytic system could be efficiently reused 10 times.

Pd NPs were also formed in situ in a copper- and ligand-free Sonogashira reaction in a five-component oil-in-water microemulsion of heptane/butanol/water/propylene glycol/Triton X 100 containing palladium dichloride and sodium hydroxide.²² The alcohols may act as reducing agents and the nonionic surfactant as the stabilizer. The system is very active for activated and deactivated aryl iodides but very poor conversions were achieved for aryl bromides.

A multifunctional assembly of Pd nanoparticles coordinated to a magnetite-amino functionalized silica system (Mag-SiO₂-Pd) was used as catalyst in the coupling of phenylacetylene with several aryl and heteroaryl iodides and bromides in the presence of triphenylphosphine and copper iodide as additives and diisopropylamine as base.²³ Successful recycling experiments up to the third run were performed after magnetic separation of Mag-SiO₂-Pd from the reaction mixture. The yields decreased to 17% in the fourth cycle due to detachment of Pd NPs from the silica spheres as shown by TEM observations.

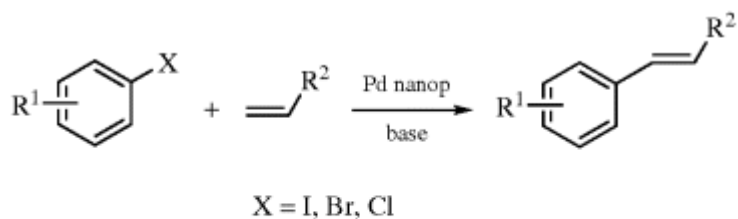
Pd NPs highly dispersed on nitrogen-doped magnetic carbon nanoparticles (N-MCNPs) by an impregnation method²⁴ were assayed as catalysts in the Sonogashira coupling of phenylacetylene with *p*-bromoacetophenone, using sodium carbonate as base, dimethyl sulfoxide as solvent, and copper iodide as additive. It is worth noting that the magnetically recoverable Pd/N-MNCs could be readily reused three times.

Polysilane-supported Pd NPs prepared by an encapsulation technique were used in the Sonogashira coupling of iodobenzene with phenylacetylene in the presence of potassium carbonate in ethanol at 80 °C. No recycling was mentioned for this process.²⁵

Heck Reactions

Pd NPs have been largely employed in the last years as catalysts in the Mizoroki-Heck reaction between alkenes and haloarenes (Scheme 2). The classical conditions for this reaction are the use of a base (Et₃N, NaOAc, ...) in polar solvents (DMF, NMP) at high temperatures (130–150 °C) in the presence of a Pd(II) source and ligands (usually phosphines) that stabilized Pd(0) species formed during the reaction. Elimination of toxic and unrecoverable phosphines would be desirable to extend this reaction to industry, and Pd NPs can be good substitutes.

Scheme 2.



R¹ = CH₃, NO₂, COMe, COPh, CHO, OMe, CH₂OH, NHCOMe, I, Br

R² = COOMe, COOEt, COOBu, COOH, CN, Ph

Several groups have observed the in situ formation of Pd NPs under classical Heck conditions in the presence of different Pd(II) sources,²⁶⁻²⁸ which seem to be the real catalysts or the precursors of leached Pd catalytic species.¹⁹ Heck reactions have also been performed in water at room temperature under ultrasonic irradiation, in the presence of Na₂CO₃, tetrabutylammonium bromide (TBAB) and PdCl₂, with Pd NPs being formed in situ. Several coupling reactions between methyl acrylate and aromatic polyiodides were studied, and high regioselectivity was observed.²⁹ A model reaction was studied to recover and reuse the catalyst retained in water; good results were obtained after four cycles.

1,5-Bis(4,4'-bis(perfluorooctyl)phenyl)1,4-pentadien-3-one stabilized Pd NPs were efficient recoverable catalysts under fluoruous biphasic conditions (5 cycles) for the reaction between phenyl iodide and several mono and disubstituted alkenes for five consecutive runs.³⁰

15-Membered triolefinic macrocycles containing in their structures polyfluorinated and polyoxyethylenated chains, and their corresponding Pd(0) complexes, had the ability to stabilize Pd NPs (2.9–5.6 nm).³¹ The Mizoroki–Heck reaction between iodobenzene and *n*-butyl acrylate gave good conversions after five consecutive runs, when treated in a closed reactor in THF at 90 °C in the presence of Bu₃N. The catalytic materials were easily recovered by filtration at the end of the reaction; the polyoxyethylenated macrocycles precipitated upon addition of diethyl ether, and the perfluorinated ones were insoluble in cold CH₃CN.

Several groups have reported the stabilization of Pd NPs by polymers. These materials are usually robust, recyclable and highly active in homogeneous or heterogeneous catalysis. Pd NPs, obtained by the metal vapor synthesis technique, were deposited on very stable polydimethylphosphazene (PDMP).³² The reaction between iodobenzene and methyl acrylate in NMP at 75 °C in the presence of triethylamine was homogeneously catalyzed by this material. The catalyst could be recovered from the reaction mixture by precipitation with diethyl ether or THF and reused four times with no significant reduction in activity and selectivity. Pd NPs stabilized by styrene-divinylbenzene polymers were active in Heck reactions; however, the activity was lost upon recycling.¹⁴ Poly(aniline)-supported Pd NPs were also effective catalysts for the Heck reaction of aryl iodide with acrylates and styrene.³³

Poly(ethylene glycol) (PEG),³⁴ poly(ethylene oxide) and poly(ϵ -caprolactone) copolymer,³⁵ optically active amphiphilic hyperbranched polyglycerols,³⁶ and polyvinylpyrrolidone (PVP)³⁷ have also been used as stabilizers of Pd NPs for Heck reactions. PEG stabilized Pd NPs were used as recyclable catalysts for Heck reaction of activated and deactivated aryl iodides and bromides, in the presence of K_3PO_4 as base, for more than six runs without obvious deactivation.³⁴ PVP stabilized Pd NPs in $(Bu_4N)(Br)$ medium were catalytically active in the Heck coupling of bromobenzene with butyl acrylate.³⁷ Several bases were tested, such as Et_3N , $NaHCO_3$, $HCOONa$, the last one being the more active, even in the fourth cycle.

Pd NPs can also be stabilized within micelles formed, in most cases by the presence of copolymers containing hydrophobic and hydrophilic parts.³⁵⁻⁴¹ A copolymer obtained from styrene, 2-((2-phenylallyloxy)methyl)oxirane and tetraethylene glycol mono-2-phenyl-2-propenyl ether in the presence of AIBN, stabilized Pd NPs. They catalyzed the Heck reaction in the presence of K_2CO_3 in NMP at 120 °C.³⁸ Pd NPs stabilized by micelles of polystyrene–poly(ethylene oxide) copolymer with cetylpyridinium chloride (a cationic surfactant), were also used to catalyze this type of reaction in DMA in the presence of NBu_3 .³⁹ Addition of PPh_3 or Bu_4NBr increased the product yield and the rate of the reaction. The recovery and recycling of the catalyst was possible using a thermomorphic heptane-10% aqueous DMA (2:1) mixture as the reaction medium (biphasic catalysis). After three cycles no change in activity and no palladium black formation was observed. Pd NPs stabilized by polysilane shell cross-linked micelles⁴⁰ or Triton X10 (oligo (ethylene glycol) (10) mono-octylphenyl ether, TX10) in heptane/butanol/water/propylene glycol microemulsions⁴¹ were also good catalysts for simple Heck reactions.

Pd NPs encapsulated in dendrimers have also been used as homogeneous recoverable catalysts in Heck reactions in the absence of toxic phosphines. Poly(propylene imine) (PPI) dendrimers, bearing covalently attached perfluorinated polyethers on the surface, acted as templates for the formation and entrapment of nanoscopic Pd NPs. These materials catalyzed the coupling of unactivated aryl halides with butyl acrylate at 90 °C in a highly selective manner (100% *trans* product) and in an environmentally friendly reaction biphasic system (organic/perfluorinated solvents). The catalyst was easily recovered and reused without loss of activity.⁴² The same type of material has catalyzed the reaction of methyl acrylate with iodobenzene at 75 °C in supercritical CO_2 ($scCO_2$), in a homogeneous manner, to form methyl 2-phenylacrylate selectively.⁴³ Christensen showed how hydroxy-terminated PAMAM-dendrimers containing encapsulated Pd NPs catalyzed this type of reaction in polar solvents (DMF or DMA) using a very small amount of palladium (0.025%).⁴⁴ Pd NPs could also be protected by dendrons linked to them by covalent bonds between surface palladium atoms and thiolate groups on the core of dendrons. This material efficiently catalyzed the coupling reaction between iodobenzene and alkenes in toluene in the presence of triethylamine. The reaction was performed in a homogeneous manner and the catalyst was recovered by filtration, after evaporation of toluene and extraction of the products with diethyl ether, in which the nanoparticulated material was not soluble.⁴⁵

Pd NPs supported on layered double hydroxide (LDH)¹² were good heterogeneous catalysts for Heck olefinations of nonactivated chloroarenes when treated with Bu_3N in nonaqueous ionic liquids (NAIL) in the presence of tetra-*n*-butylammonium

bromide. Long reaction times (10–40 h) could be dramatically reduced under microwave irradiation (0.5–1 h). A higher turnover frequency for chlorobenzenes was obtained (63.3 h^{-1}) when compared to the results obtained using homogeneous PdCl_2 in ionic liquids (0.39 h^{-1}). Pd NPs stabilized by LDH were reused for five cycles to record a global TON of 160. The catalyst was recovered in the NAIL phase after vacuum distillation of the reactants and products at the end of each reaction.

Nanoparticles stabilized by polyoxometalates were found to be versatile catalysts for C—C and C—N coupling reactions.⁴⁶ Heck-type coupling between both styrene and methyl acrylate, as alkenes, and bromoarenes (e.g., 4-bromotoluene) and activated chloroarenes (e.g., 1-chloro-4-nitrobenzene) were performed. Classical reaction conditions were followed (substrate:alkene:diisopropylamine:catalyst, 1:2.5:3:0.01, in water:ethanol 4:1 at $80 \text{ }^\circ\text{C}$, 16 h) and quantitative yields were obtained.

Silica, titania, alumina, aerogels, zeolites, and carbon nanotubes are also good stable supports for Pd NPs, giving easily recoverable heterogeneous catalysts with high surface areas. SiO_2 -supported Pd NPs were an excellent catalyst for Heck reaction of bromobenzene and styrene, being recovered and reused (3 runs).⁴⁷ Its activity was comparable to that of homogeneous Pd systems [$\text{Pd}(\text{acac})_2$ or $\text{Pd}(\text{OAc})_2$].

Highly dispersed palladium colloids were prepared in a modified mesoporous SBA-15 material.⁴⁸ The catalytic activity of this material was investigated for the reaction between activated and nonactivated aryl halides, with styrene and methyl acrylate. The reactions were carried out in air at temperatures between 120 and $170 \text{ }^\circ\text{C}$, in NMP using Et_3N as base. The catalyst could be recovered by simple filtration and reused without any apparent decrease in its catalytic activity.

A new recoverable palladium catalyst based on a magnetic body of silica-coated Fe_3O_4 has been prepared and used for six runs in coupling reactions of iodobenzene, acrylic acid in $\text{CH}_3\text{CN}/\text{water}$ in the presence of NaOAc as a base, at reflux. Good results were obtained in the first run, but a decrease of its activity was observed in the next ones. The catalyst was separated from the reaction medium under an external magnetic field.⁴⁹

Palladium(II) complexes of polydimethylsiloxane-derived phosphine ligands [$\text{Pd}(\text{PDMS-PPh}_2)_2\text{Cl}_2$] have been adsorbed onto silica through hydrogen bonding and van der Waals interactions. This material acted as a precatalyst in Heck reactions.⁵⁰ When 4-iodotoluene, methyl acrylate, and *N,N*-diisopropylethylamine were added to the modified silica material (2% of Pd) in toluene or in scCO_2 , the desired coupling product was obtained in good conversions. In both cases, the catalyst could be recovered and reused several times; however, in toluene more leaching was observed and recycling gave worse results. The analysis of the material after reaction in scCO_2 revealed the presence of agglomerated Pd NPs, which were considered the real catalyst of these reactions.

A combination of mixed monolayer protected palladium clusters (Pd MMPC) with SiO_2 , both systems functionalized with acid groups, with an amino-functionalized polystyrene, gave, by an electrostatically-mediated assembly process and subsequent calcination, a material containing well-dispersed Pd NPs.⁵¹ Its activity in Heck catalysis of activated and electronically neutral bromoarenes with alkenes was higher

than commercially available Pd/C and Pd/SiO₂, and it could be recycled with only a small decrease in activity.

The sol-gel process is another way to incorporate palladium nanoparticles in silica or titania materials. Pd NPs were generated from Pd(PPh₃)₄ in a mixture of tetra(ethylene glycol) and tetramethoxysilane (or titanium (IV) isopropoxide), then encapsulated in a silica or titania matrix by treatment with water.¹³ This material was an effective catalyst for the activation of aryl iodides and aryl bromides, but it was not active enough to perform Heck reactions with aryl chlorides.

Inorganic, organic, and carbon aerogels have been used to encapsulate and stabilize Pd NPs.^{52,53} All three materials were used as Heck catalysts, the organic and carbon aerogels being the most active. Carbon aerogel was recovered and reused five times, and no leaching was detected.⁵² The use of ionic liquids in the preparation of well-dispersed Pd NPs inside an aerogel was described by the group of Marr.⁵⁴ The solid containing Pd NPs was used as a catalyst for a common Heck reaction in DMF using Et₃N as base. It was recovered and reused, with higher reaction times in the second run. Pd NPs stabilized in Al₂O₃ catalyzed, in a heterogeneous manner, the coupling reaction between bromobenzene and butyl acrylate in the presence of Bu₄NBr. Depending on the base used (NaHCO₃, NaOAc, NBu₃) mono or diarylated products were obtained. The catalysts could be recovered, giving 100% conversion after the fifth run.⁵⁵

Functionalized Na-Y zeolites containing Pd NPs on their surface were good catalysts for a Heck reaction between iodobenzene and styrene performed in DMAC in the presence of Et₃N, giving mixtures of *cis* and *trans*-stilbene. The catalyst was easily recovered and it was reused three times without loss of activity.⁵⁶ Pd-trapped zeolitic microcapsular reactors showed high activity as catalysts in Heck reactions.⁵⁷ The reaction between iodobenzene with methyl acrylate was performed quasi-homogeneously inside the reactor, but at the end of the reaction Pd NPs were retained inside. More than 10 recyclings have been performed without loss of activity, and leaching was negligible.

Corma and co-workers have deposited Pd NPs on single wall carbon nanotubes (SWNT).⁵⁸ These materials were tested as Heck catalysts in DMF at 150 °C using NaOAc as base. Although an important leaching was observed during the reaction, the catalytic activity was maintained, a fact that could be explained by the re-deposition of most of the Pd NPs on the SWNT at the end of the reaction (boomerang effect).

Also natural porous materials, such as diatomite, have been used as Pd NP stabilizers. Many Heck reactions were tested, mainly between aryl iodides and different alkenes, giving good results. The heterogeneous catalyst could be easily recovered. The study also revealed that the palladium leaching into the solution during the reaction provided the real catalytic species.⁵⁹

In the last years the use of ionic liquids as “green solvents” in organic reactions has been developed. These solvents are mainly quaternary ammonium salts, pyridinium, and imidazolium salts. The formation in situ of Pd NPs was observed by Srinivasan after fast Heck reaction of iodobenzene and ethyl acrylate in 1,3-di-*n*-butylimidazolium tetrafluoroborate catalyzed by a Pd-biscarbene complex under

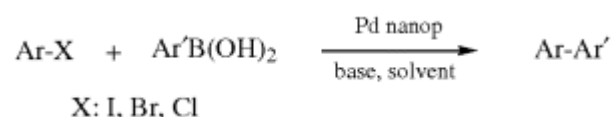
ultrasonic irradiation at 30 °C.⁶⁰ Calò and co-workers have studied Heck reactions catalyzed by Pd NPs of aryl iodides and bromides and also activated aryl chlorides with a large variety of mono- and disubstituted alkenes in ionic liquids. The regio- and stereospecificity depended on the type of precatalyst, ionic liquid, and base used. However, recovery and reuse was not successful.⁶¹ Better results were obtained when Pd NPs were prepared in the presence of chitosan (poly((1-4)-2-amino-2-deoxy-D-glucan()), a cheap natural polymer. With this system, Heck reactions with iodobenzene could be performed for 11 cycles in very good conversions.⁶² The role of ionic liquid-stabilized Pd NPs in the Heck reaction of aryl halide and butyl acrylate has also been studied by Dupont.⁶³ Organic products were extracted with ether after reaction and no nanoparticles were observed in that phase. The ionic liquid was a Pd NP reservoir.

It has recently been described that triphasic solvent systems are capable of generating highly dispersed Pd NPs that are active and selective for catalysis. Isooctane, water, and trioctylmethylammonium chloride/decanol promoted the formation of Pd NPs, from Pd(PPh₃)₄, which remained immobilized in the onium phase.⁶⁴ Phenyl iodide and ethyl acrylate were reacted at 80 °C in this mixture, using NaHCO₃ as base.

Suzuki Cross-coupling Reactions

Palladium-catalyzed coupling of aryl halides with aryl boronic acids is a useful method for the synthesis of unsymmetrical biaryls (Scheme 3). The formation of nanoparticles involves different stabilizers that not only shield the metal core but also sterically inhibits its access.

Scheme 3.



Pd NPs can be prepared by electrostatic stabilization including steric protection. For instance, Pd NPs stabilized by tetraalkylammonium salts bearing long alkyl chains have been used as catalysts in quaternary ammonium salts as solvent by the group of Nacci.⁶⁵ Recycling experiments carried out with *p*-bromotoluene showed that the catalytic system can be reused three times.

Some of the protecting agents that prevent agglomeration of the metallic cluster provide steric stabilization through a functional group with high affinity for palladium including thiols, amines, phosphines, and sulfides. Astruc's group has investigated⁶⁶ the catalytic properties of simple dodecanethiolate Pd NPs showing remarkable efficiency (ArX, X: Cl, Br, I) and recyclability (six times). Synthesis of small nanoparticles (1.2 nm) has been achieved using a bisphosphine BINAP bearing a sulphur alkyl chain.⁶⁷ Kaifer⁶⁸ has also investigated the catalytic properties of Pd NPs derivatized with surface attached perthiolated cyclodextrin receptors. Furthermore,

palladium colloids soluble in perfluorinated solvents can be obtained using 1,5-bis(4,4'-bis(perfluorooctyl)phenyl)-1,4-pentadien-3-one as stabilizer, and used as efficient recoverable catalysts in a Suzuki coupling under fluoruous biphasic conditions.³⁰

Pd NPs can also be stabilized by incorporation into polymers. Extensive work has been based on the use of organic polymers. For example, Park's group¹⁴ has generated Pd NPs from Pd(PPh₃)₄ and polymer precursors under an oxygen balloon, with subsequent radical polymerization. The group of El-Sayed^{69, 70} has studied the effect of the catalytic reaction on the stability of metallic NPs. Pd NPs were prepared from H₂PdCl₄ and poly(*N*-vinyl-2-pyrrolidone) (PVP) in a reducing ethanolic solution. They conclude that phenylboronic acid binds to the surface of the Pd NPs and iodobenzene does not. Furthermore, a series of PVP-stabilized Pd NPs with varying particle size were prepared, and an increased catalytic activity with a decrease in particle size was found on the catalytic Suzuki reactions in aqueous solution.^{70, 71} Others⁷² have prepared PVP-Pd NPs that are known to bind to silicon nitride, and catalytically functional AFM probes were generated by incubating precleaned silicon nitride probes in an aqueous solution of PVP-Pd NPs. The AFM probe is used as a mediator of Suzuki coupling reactions. Recently, the group of Hyeon⁷³ has used triblock Pluronic copolymers [poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide)] as capping agents for the synthesis of Pd NPs that showed high catalytic activity for iodo- and bromoaryl halides.

Moreover, poly(*N,N*-dialkylcarbodiimide) was found to be an effective polymeric ligand system for Pd NP's (1–5 nm).⁷⁴ The catalytic activity and NPs aging were examined using microwave and conventional heating.⁷⁵ Bawendi⁷⁶ has developed a phosphine oxide gel using bis(dichlorophosphino)ethane and poly(ethylene glycol) that can be used to transfer NPs from organic solvents to water. The reactivity of aqueous Pd NPs was investigated using the Suzuki coupling reaction obtaining an important loss of activity in the second run. The group of Billaud³³ has prepared polyaniline-supported Pd NPs. Only aryl iodides were active in the Suzuki reaction.

The group of Garcia²⁰ has compared the use of a carbapalladacycle complex of 4-hydroxyacetophenone oxime in imidazolium ionic liquids and in poly(ethylene glycol) (PEG). They found that PEG is a very convenient method allowing the reuse of the catalyst. The decomposition of the organometallic complex occurs under reaction conditions and Pd NPs are stabilized by PEG.

Others⁷⁷ have introduced microgels as stabilizers for metal nanoclusters. Microgels can be prepared by modification of standard polymerization techniques having pendant functional groups able to interact with metal ions that can be reduced inside the microgel. Another approach is the encapsulation of palladium nanoparticles in polyurea microcapsules.⁷⁸

Bradley⁷⁹ has shown that soluble Pd(OAc)₂ can enter into swollen resins. A cross-linked resin-captured palladium was prepared by treating Pd(OAc)₂ and aminomethylated Tentagel resin (PS-PEG) and subsequent reduction with hydrazine hydrate. The resulting resin was cross-linked with succinyl chloride to fix the captured Pd NPs. This supported catalyst is predominantly heterogeneous and can be recycled.

Another kind of polymeric supports are the so-called poly-HIPE porous materials obtained by polymerization of a high internal phase reverse emulsion. These materials can be further functionalized with suitable chemical groups, such as an amine, to promote the growth of Pd NPs. Backov⁸⁰ has used this strategy and checked the materials in Suzuki reaction.

Pd NPs can also be supported on modified inorganic polymers, such as modified silicas. MCM-41 silica, whose pores have been expanded by a treatment with *N,N*-dimethyldecylamine, was used as a support for the preparation of NPs.⁸¹ Then the materials were calcinated and hydrogenated, showing high activity and no leaching (4 cycles). In addition, a mesoporous commercial Kieselgel 100 silica was modified via attachment of different organosiloxanes, and then Pd(OAc)₂ was immobilized on the silica.⁸² Materials were studied in the Suzuki reaction of 4-bromoanisole observing palladium leaching after 4–6 runs. Metal complexes of polydimethylsiloxane-derived ligands can be absorbed onto silica and subsequently reduced in situ (Suzuki reaction conditions) in scCO₂ to generate NPs.^{50a} The use of scCO₂ prevents the desorption of the Pd NPs from their support, and the catalyst can be reused several times. Hyeon⁸³ has prepared hollow spheres composed of Pd NPs. The method consists of the synthesis of uniform silica spheres that are functionalized with mercaptopropylsilyl groups, then Pd (acac)₂ is absorbed and heated at 250 °C. The CO generated from the thermal decomposition seems to act as reductant. These heterogeneous catalysts can be recycled seven times. Others have supported Pd NPs (20–100 nm) on natural diatomite.⁵⁹ A series of aryl bromides and iodides gave excellent yields in Pd-diatomite catalyzed Suzuki reaction. The group of Park¹³ have generated Pd NPs from Pd(PPh₃)₄ in a mixture of tetra(ethylene glycol) and tetramethoxysilane and then encapsulated in a silica matrix. The resulting heterogeneous material showed activity with aryl bromides and iodides.

Besides silica's, other oxides and hydroxides have been used to immobilize Pd NPs. Choudary¹² and Kantam⁸⁴ described the use of Mg–Al layered double hydroxides as the material of choice not only to stabilize Pd NPs but also to provide the adequate electron density to Pd(0) to facilitate the oxidative addition of bromo-, iodo- and chloroarenes. Excellent results were obtained in the Suzuki reaction for aryl chlorides. The same groups⁸⁵ have used a catalyst prepared by counterion stabilization of PdCl₄²⁻ with nanocrystalline MgO followed by reduction with an excess of hydrazine hydrate. This material exhibits excellent activity in Suzuki cross coupling of haloarenes (chloro, bromo and iodo) and can be recycled and reused for four cycles. Pd Nps (15–20 nm) stabilized by Keggin-type polyoxometalates were prepared by reduction of K₅PPdW₁₁O₃₉ with H₂. Chloroarenes were also reactive in this reaction media without solvent.⁴⁶ Moreover, a hydroxyapatite-bound palladium complex was synthesized by Kaneda's group. The complex catalyzed the coupling of aryl chlorides in the presence of TBAB, and under such conditions Pd NPs were generated on the surface of the hydroxyapatite.⁸⁶

Carbon-supported Pd NPs have been prepared by adsorption of PVP-Pd NPs onto activated carbon⁸⁷ or by deposition of spontaneously reduced Pd(OAc)₂ on single wall carbon nanotubes.⁵⁸ Recently Pd NPs have been deposited on nitrogen-doped magnetic carbon NPs by a simple impregnation method.²⁴ The catalytic performance of these carbon-supported Pd-NPs has been investigated for Suzuki coupling

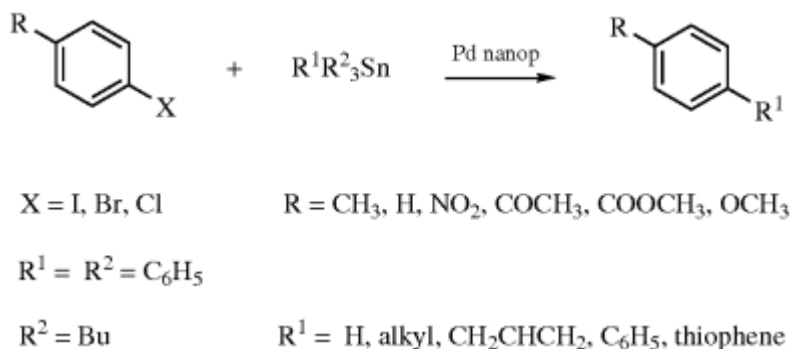
reactions.

Dendrimers are attractive hosts for metal NPs and some groups have investigated dendrimer-encapsulated Pd NPs. For instance Astruc⁸⁸ studied fifth generation amino terminal dendrimers [DAB(diaminobutane)dendrimers] in the formation of Pd NPs. Christensen⁸⁹ investigated fourth generation polyamidoamine dendrimers (PAMAM G4-OH) and Fan⁹⁰ studied third generation phosphine dendrimers. Recently Fox and co-workers⁴⁵ reported the use of Pd NP-cored third generation dendrimers as catalysts in Suzuki reactions. The materials were prepared from K_2PdCl_4 , tetraoctylammonium bromide and a Fréchet-type dendritic polyaryl ether disulfide. Finally, El-Sayed^{70,91} has compared the activity of Pd NPs prepared in the presence of three different stabilizers: PVP, block copolymer and G3 dendrimer. The stability of NPs is controlled by the type of the stabilizer, the reactants, and the base used in the Suzuki reaction.

Stille Cross-coupling Reactions

Some examples of coupling reactions between haloarenes and tin derivatives (Stille cross coupling) catalyzed by palladium nanoparticles have been described (Scheme 4). Pd NPs stabilized by polyoxometalates effectively catalyzed the coupling reaction between 4-bromotoluene and 1-chloro-4-nitrobenzene with tetraphenyltin in water-DMF 1:1 at 110 °C in the presence of diisopropylamine.⁴⁶

Scheme 4.



Some ionic liquids based on the *N*-butyronitrile pyridinium cation have been used as solvents for palladium-catalyzed biphasic Stille coupling reactions.⁹² The reaction of iodobenzene with phenyltributylstannane in the ionic liquid, in the presence of Pd(II) complexes (5%) at 80 °C, gave the corresponding biphenyl derivatives. TEM analysis of the ionic liquid after the reaction showed that the real catalysts were Pd NPs formed in situ. Catalyst recycling experiments were performed; the product yield was essentially unchanged even after the ninth catalytic cycle.

A more extended work has been published by Nacci,⁶⁵ where several aryl bromides and chlorides (some of them non activated) have been coupled with

tributylphenylstannane in ionic liquids. Mild conditions were used and neither bases nor other additives were required. Pd NPs were previously prepared, then aryl halide and tributylphenylstannane were added and stirred at 90 °C. High product yields were obtained when aryl bromides were used; however, modest yields of the corresponding biaryls were obtained for deactivated electron-rich aryl chlorides, even working at higher temperatures (110–130 °C). The mixture solvent/catalyst was recycled five times with little loss in activity. The coupling of methyl 4-iodobenzoate with tributylvinyltin in the presence of CsF in dioxane at 120 °C was catalyzed by Pd NPs entrapped in silica gel.¹³

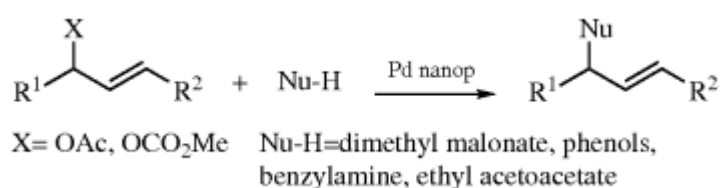
Chouday reported for the first time Stille-type couplings of deactivated chloroarenes with trialkyltin reagents with heterogeneous Pd NPs stabilized by layered double hydroxide (LDH).¹² Various chloroarenes were coupled with 2 equiv of tributyltin hydride at 50 °C in the presence of a catalytic amount of the LDH-Pd⁰ using potassium acetate as a base and NMP as solvent, to afford selectively the corresponding trialkylarylstannanes. The catalyst was reused for five cycles, maintaining its activity and selectivity.

More recently, Fujihara⁶⁷ has described the preparation of Pd NPs stabilized by 6-octyl-substituted BINAP (C₈-BINAP). This material catalyzed the coupling reaction between methyl 2-iodobenzoate and 2-(tributylstannyl)thiophene at room temperature, giving the desired product in good yield. Pd NPs were recovered and reused without loss in activity.

Tsuji–Trost Allylation Reactions

Some few recent examples of alkylation of nucleophiles with allylic acetates or carbonates (Tsuji–Trost allylation) catalyzed by palladium(0) nanoparticles (Pd NPs) have been described (Scheme 5).

Scheme 5.



The enantioselective allylic alkylation of *rac*-3-acetoxy-1,3-diphenyl-1-propene with dimethyl malonate has been performed with Pd NPs stabilized by a chiral xylofuranoside diphosphite,⁹³ which were obtained by decomposition of Pd₂(dba)₃ by H₂ (3 bar) in the presence of the ligand (Pd/ligand = 1/0.2). The allylation reaction under basic conditions (BSA, KOAc) in dichloromethane at room temperature did not proceed to completion after prolonged reaction times, and a very high kinetic resolution of the substrate was observed in addition to high enantiomeric excess (97%) for the final product. In contrast, quasi total conversion at short reaction times but no kinetic resolution was achieved in the same reaction with a molecular complex

generated in situ from $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$ and the diphosphite chiral ligand.

Palladium nanoparticles dispersed in cross-linked polystyrene¹⁴ catalyzed the reaction of phenols and naphthols with allyl methyl carbonate in THF at 70 °C in the presence of triphenylphosphine. Recycling was not mentioned.

Regioselective allylic amination of cinnamyl acetate with benzylamine has been reported⁹⁴ in THF at room temperature with Pd NPs immobilized in mesoporous thin silica films, only the linear compound being obtained. Surprisingly, the reaction under homogeneous conditions is much slower and less regioselective, affording a 3:1 mixture of linear and branched compounds. The authors relate both features to the so called confinement effects. One re-use has been reported.

Kaneda has recently described⁹⁵ the preparation of stable subnanoordered Pd clusters (< 1 nm) entrapped within the sterically restricted interlamellar spaces of a montmorillonite (mont). Alkylation of methyl allyl carbonate was performed with this heterogeneous recyclable system with ethyl acetoacetate and *p*-nitrophenol as nucleophiles in ethanol and water as solvents at 80 °C. Recycling has been reported for the C-nucleophile, three consecutive cycles being achieved with no decrease of yield and no palladium aggregation. A deleterious effect was observed upon addition of triphenylphosphine. This Pd catalyst under organic-ligand-free conditions gave much better results than other heterogeneous systems such as Pd/Al₂O₃, Pd/SiO₂, Pd/C, Pd/TiO₂ or homogeneous systems such as Pd(PPh₃)₄. The use of Pd-mont in the allylation of *cis*-3-acetoxy-5-carbomethoxycyclohex-1-ene with ethyl acetoacetate provided superior selectivity toward the *cis* product compared with Pd(PPh₃)₄.

Hydrogenation and Hydrogenolysis Reactions

The hydrogenation of unsaturated hydrocarbons on Pd NPs is one of the best studied catalytic applications of palladium clusters. The colloids can be prepared using a large number of stabilizers and applying different methods and have been successfully used as catalysts for the H₂ reduction of alkenes.^{43, 51, 96-119} Some studies on alkene hydrogenation are focused on the preparation of recyclable Pd NPs,¹²⁰⁻¹³² while others put the aim in selective processes,^{58, 133-153} including alkene hydrogenation in the presence of other reducible functional groups. Some works describe catalysts active for both hydrogenation of alkenes and alkynes.^{13, 14, 25, 56, 154-161} Interestingly, a lot of research groups have studied hydrogenation methods for the selective conversion of alkynes into alkenes.¹⁶²⁻¹⁷⁵

Pd NPs prepared by several procedures using a variety of stabilizers have also been successfully used as catalysts for the hydrogenation of other organic substrates, apart from alkenes and alkynes, such as arenes and heteroarenes (partial or complete hydrogenation of the aromatic ring),^{38, 104, 160, 176-179} carbonyl compounds (hydrogenation of C=O),^{25, 104, 116, 128, 153, 159, 180, 181} nitro derivatives,^{25, 56, 123, 128, 140, 154, 176, 182-184} aryl halides (dehalogenation),^{64, 178, 185-187} hydrogenolysis of epoxides to give alcohols,^{162, 188, 189} hydrogenolysis^{25, 179, 190} of benzyl ethers and O-benzyl carbamates, deoxygenation of benzylic alcohols to give alkanes,¹⁴⁰ nitriles,¹⁰⁴ imines¹⁵⁰ (hydrogenation of C=N), aryl azides,¹⁵⁴ and 2-ethylanthraquinone.^{123, 191} Chemoselective hydrogenation of 2-ethylanthraquinone to 2-ethylanthrahydroquinone is a key step in the current industrial synthesis of hydrogen peroxide.

Other Reductions

Dendrimer-palladium nanocomposites have been used in the catalytic reduction of *p*-nitrophenol to *p*-aminophenol with sodium borohydride.¹⁹² Kinetic studies for the nitroarene reduction showed that the rate constants for the PPI dendrimer-palladium nanocomposites are greater than those for the PAMAM dendrimer nanocomposites, a fact that has been attributed to a much faster diffusion of the substrate to the metal nanoparticle surface for the PPI dendrimer than the PAMAM dendrimer. The same reaction has also been performed with Pd NPs encapsulated in spherical polyelectrolyte brushes (SPB) and core-shell microgels.¹⁹³ The measured rate constants for the reduction of *p*-nitrophenol with both catalytic systems demonstrated that the Pd NPs immobilized in the brush particles exhibited a much higher activity than those immobilized within the microgel particles, due to a better diffusion of the reactants in the SPB carrier system.

Catalytic reduction of nitro-substituted arenes and heteroarenes to the corresponding amines has been carried out using a combination of palladium(II) acetate, aqueous potassium fluoride and polymethylhydrosiloxane (PMHS) in THF at room temperature.¹⁹⁴ Replacing PMHS/KF with triethylsilane allows aliphatic nitro derivatives to be reduced to their corresponding hydroxylamines. Palladium(0) nanoparticles are the catalytic species generated in situ, silanes and siloxanes acting as reducing and stabilizing agents.

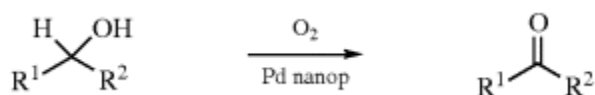
Polyurea-microencapsulated Pd NPs¹⁸⁸ have been used as efficient and recyclable catalyst for reductive ring opening of benzylic epoxides using HCOOH/Et₃N as a hydrogen donor in ethyl acetate at room temperature, the homobenzylic alcohols being obtained regioselectively. Recycling experiments were performed with *trans*-stilbene oxide, 10 successive runs being achieved without any loss of activity.

Amphiphilic polystyrene-poly(ethylene glycol) (PS-PEG) resin dispersion of Pd Nps exhibited a high catalytic performance in the hydrodechlorination of substituted chloroarenes under aqueous conditions. The process took place smoothly at room temperature using aqueous ammonium formate as the hydrogen source with high recyclability (10 cycles without loss of activity).^{142, 195}

Catalytic Aerobic Alcohol Oxidation

Catalytic aerobic alcohol oxidation of alcohols to aldehydes and ketones is being intensively investigated to replace stoichiometric oxidation processes that generate large amounts of heavy metal and solvent waste and to find much cheaper, safer, and more environmentally benign oxidation protocols. Several groups have recently developed nanopalladium catalysts for this fundamental chemical transformation (Scheme 6). Many of them use water as solvent under an atmospheric pressure of oxygen, although oxidations in organic solvents and in supercritical carbon dioxide (scCO₂) have also been performed.

Scheme 6.



Leitner has reported¹⁹⁶ the selective continuous-flow biphasic aerobic oxidation of benzylic and allylic alcohols catalyzed by poly(ethylene glycol)-stabilized Pd Nps in scCO₂ (d CO₂/O₂ = 0.55 g/mL, 65–80 °C). Primary and secondary aliphatic alcohols require some longer reaction times. Oxidation of 1-butanol is not selective, affording butyric acid as the main product. The use of scCO₂ as a reaction medium allows efficient recycling (4 runs) with benzyl alcohol.

Later on, this author¹⁹⁷ has performed the same reaction by Pd Nps stabilized on PEG-modified silica in scCO₂. The solid inorganic matrix allows the use of simple and highly efficient fixed-bed technology and reduces the risk of oxidative degradation of a pure PEG-matrix. Comparison with noncovalently modified silicas clearly demonstrated the beneficial effect of the covalently bound PEG phase. Pd Nps immobilized in the mesoporous channels of a bipyridyl-functionalized SBA-15 have been described as a highly efficient heterogeneous recoverable catalyst for aerobic oxidation of benzylic, allylic and secondary aliphatic alcohols.¹⁹⁸ Primary alkanols give esters as main products. The reaction was performed in air or under an atmospheric pressure of oxygen, in toluene at 80 °C in the presence of 1 equiv of K₂CO₃. Efficient recycling (12 runs) is favored by the bipyridyl ligand, which is effective for both preventing the leaching of palladium species and the agglomeration of coordinated palladium nanoparticles. *In situ* formation of Pd nanoclusters (2–4 nm) was observed in the aerobic oxidation of benzyl alcohol to benzaldehyde performed in toluene at 80 °C with Pd(OAc)₂ in the presence of a silasesquioxane-pyridyl ligand.¹⁹⁹

Other inorganic supports for Pd Nps have also been employed in this type of reaction. Oxidation of glycerol in water has been accomplished with Pd nanoparticles (4–5 nm) (5 wt%) supported on graphite and activated carbon in a batch reactor at 60 °C and 1 bar pressure using air as the oxidant or in an autoclave with pure oxygen at 3 bar pressure.²⁰⁰ This is a challenging process due to the large number of possible oxidation compounds. Some selectivity to glyceric acid was obtained, but C2 and C3 side-products were present. Corma and Garcia⁵⁸ have found that, in contrast to the Heck and Suzuki reactions, Pd/C is more active than Pd NPs deposited on single wall carbon nanotubes (SWNT) for the catalytic oxidation of cinnamyl alcohol to cinnamaldehyde by molecular oxygen in ethanol at 80 °C. Ordered mesoporous carbon containing molecular-level dispersed Pd clusters (< 1 nm) in the carbon walls synthesized by the nanocasting pathway showed high selectivity for the aerobic oxidation of benzylic and allylic alcohols in scCO₂ as reaction medium at 80 °C.²⁰¹ The catalyst was found to be reusable. Hydroxyapatite-supported Pd nanoclusters²⁰² promoted the oxidation of allylic and benzylic alcohols and α -hydroxy ketones under an atmospheric oxygen pressure at 90 °C, in trifluorotoluene or under solvent-free conditions. Recycling was possible (three cycles), and the system exhibited better performance than Pd/C, Pd/Al₂O₃ and Pd/SiO₂. Pd NPs entrapped in aluminium hydroxide¹²⁰ catalyze the oxidation of aromatic and heteroaromatic benzylic alcohols,

and secondary aliphatic alcohols, being in effective for primary alkanols. The reaction takes place in some organic solvents or in water (80–100 °C), and the catalyst can be reused 10 times without activity loss.

Organic polymers have also been used as stabilizers to provide access to Pd Nps active in catalytic aerobic oxidation of alcohols. Thus, Uozumi reported^{195, 203} the preparation of amphiphilic bipyridyl-functionalized PS-PEG resin-supported Pd Nps, which were used for the selective oxidation of allylic, primary, and secondary benzylic alcohols to the corresponding carbonyl compounds in refluxing water. Primary aliphatic alcohols gave the carboxylic acids. Efficient recycling (4 runs) was achieved for cyclooctanol. Pd nanoclusters stabilized by *N,N*-dimethylacrylamide-based soluble cross-linked polymers (microgels) were good catalysts for aerobic oxidation of benzylic alcohols but not for secondary aliphatic alcohols in water at 100 °C.²⁰⁴ Decreasing activity was found on repeated use (3 runs). Corain²⁰⁵ has chosen moderately cross-linked copolymers of *N,N*-dimethylacrylamide, 2-(methylthio)ethyl methacrylate and *N,N*-methylenebisacrylamide for the size-controlled formation of palladium nanoclusters, which showed moderate activity and selectivity for the oxidation of *n*-butanol to *n*-butanal (3 atm O₂, water, 70 °C). The same author²⁰⁶ reported similar gel-type resin/Pd nanoclusters systems by substituting the functionalized monomer 2-(methylthio)ethyl methacrylate for acrylonitrile. Moderate activity and selectivity was achieved for the oxidation of benzyl alcohol (1 bar O₂, water, K₂CO₃, 100 °C) and *n*-butanol (3 bar O₂ under analogous conditions), with mixtures of alcohol, aldehyde and acid being formed. Pd Nps dispersed in polystyrene-divinylbenzene polymer¹⁴ was a recyclable (3 runs) heterogeneous catalyst for the aerobic oxidation of benzylic alcohols in toluene at 80 °C. Aliphatic alcohols failed to react.

Other Reactions

An enantiopure *syn*-benzocyclootrimer was prepared through regioselective cyclootrimerization of an enantiopure halonorbornene derivative under palladium nanocluster conditions (a mechanism similar to that of Heck reaction was considered). The reaction was performed in 1,4-dioxane, using Bu₄NOAc and Na₂CO₃ in the presence of Pd(OAc)₂ and PPh₃. The amount of Bu₄NOAc was crucial, indicating that it played an important role in the stabilization of the Pd NPs generated in the reaction mixture, forming a well-dispersed system.²⁰⁷

Beletskaya also used palladium colloids stabilized by block copolymer micelles as an efficient catalyst for C-heteroatom bond formation (C—N, C—O) to prepare indoles and isocoumarins.³⁹ The reaction of phenylacetylene with a protected *o*-iodoaniline proceeded as a cascade process of Sonogashira coupling followed by cyclization. A related heterocyclization of methyl *o*-iodobenzoate with diphenylacetylene led to the formation of substituted isocoumarins. In both cases, the catalyst was reused three times, giving good yields.

Other cross-coupling reactions have also been promoted by Pd NPs. Thus, coupling of pyrrolidine with 4-bromotoluene and 1-chloro-4-nitrobenzene was also catalyzed by Pd NPs stabilized by polyoxometalates.⁴⁶

Pd NPs generated in situ were selective catalysts for the cross coupling of the silanes

R₃SiH with phenyl and vinyl thioethers, forming the corresponding thiosilanes and silathianes in high yields under mild conditions. The method was applicable to phenyl thioglycosides, giving access to thiosilyl glycosides, a new class of sugar derivatives.²⁰⁸ A heterogeneous layered double hydroxide-supported nanopalladium species (LDH-Pd)²⁰⁹ catalyzed a three-component coupling reaction to prepare 1,3-butadienes.^{209b} The synthetic protocol was simple and quite practical and involved a one-pot three-component coupling of aryl iodides, internal alkynes, and terminal alkenes. The solid catalyst was recovered by simple filtration and reused without loss of activity (4 runs). The selectivity and the yield of the reaction depended clearly on the solvent and the base used, DMF:H₂O (9:1) and NaHCO₃ giving the best results.

A room-temperature catalytic alternative to the Ullmann reaction based on electroreductive homocoupling of haloarenes promoted by palladium nanoparticles in ionic liquids has been reported.²¹⁰ The solvent was reused for five cycles without a change in activity.

Chiral BINAP-Pd NP's confirmed asymmetric catalytic activity in the hydrosilylation of styrene with trichlorosilane, giving chiral 1-phenyl-1-chlorosilylethane as a single isomer.²¹¹

Pd NPs stabilized by hydrosilane polymer matrix undergo an oxidative-addition and reductive-elimination sequence with Si —H and COOH bonds to produce silyl esters (recyclable catalyst).²¹² The same group has demonstrated that Pd NPs stabilized by PMHS were selective and recyclable catalysts for alcoholysis of polyhydrosiloxane. A fair number of alcohols with diverse structures were efficiently grafted onto the polysiloxane backbone, without any side reactions and under mild reaction conditions.²¹³

Silylation of sugars by silane alcoholysis of *tert*-butyldimethylsilane (TBDMS-H) and Ph₃SiH was catalyzed by Pd NPs. It is an attractive alternative to the established silyl chloride method, a change of regioselectivity being observed.²¹⁴

Cleavage of the benzyl protecting group of esters in the synthesis of oligonucleotide peptide conjugates was accomplished by a phase-transfer hydrogenation with PVP-stabilized Pd NPs and 1,4-cyclohexadiene as the hydrogen donor.²¹⁵

Pd NPs encapsulated in carbon aerogels⁵² have been used as effective catalysts for the hydroxycarbonylation of several aryl iodides using lithium formate and acetic anhydride as an internal condensed source of CO. The catalyst was air stable and easily recovered after reaction (12 cycles).²¹⁶ Methoxycarbonylation of iodobenzene has been carried out at 90 °C using Pd-PVP colloid, Et₃N, MeOH and (Bu₄N)(Br under a CO atmosphere.^{37,217} Small Pd NPs supported in silica were shown to be active in C₂H₄ hydroformylation.²¹⁸ Acetolysis of epoxides and acetylation of phenol were catalyzed by Pd NPs stabilized by Keggin ions (phosphotungstate anions).²¹⁹

Pd NPs entrapped in aluminum hydroxide¹²⁰ were efficient recyclable catalysts for the highly selective α -alkylation of ketones with alcohols.²²⁰ Reactions were performed in toluene in the presence of K₃PO₄. The catalyst could be easily recovered by filtration or decantation and, after adding a new equivalent of the base, it could be recycled six times, retaining its activity. The same reaction was also studied by Uozumi using Pd

NPs stabilized by a solid phase.²²¹ The α -alkylation of several ketones with primary alcohols were performed at room temperature in the absence of solvent (7 equiv of water were required). The heterogeneous catalyst could be recovered by centrifugation and reused three times.

A layered double hydroxide (LDH)-supported nanopalladium(0)^{209a} species was used for the allylation of aldehydes to give moderate to good yields of homoallylic alcohols.²²² Allyl bromide or allyl alcohol in the presence of stannous chloride or allyltributylstanne were used as allylating agents. The catalyst could be recovered by simple filtration and reused (4 cycles).

α -Alkylation of various nitriles with carbonyl compounds successfully proceeded using a hydrotalcite-supported palladium nanoparticle (Pd/HT) as a multifunctional catalyst that was reused for three times giving the desired product in good yield. The alkylated nitriles were formed through an aldol reaction at base sites on the hydrotalcite surface followed by hydrogenation by molecular hydrogen on the palladium nanoparticle.¹²¹ A one-pot synthesis of α , α -dialkylated nitriles was also performed by Michael reaction of previously obtained α -alkylated nitriles with electron-deficient olefins on the base sites of the HT.²²³

Pd NPs dispersed in mesoporous molecular sieve MCM-41 were active catalysts in the condensation reaction of 2-hydroxyethylamine with an excess of *cis*-butene-1,4-diol to give *N*-(2-hydroxyethyl)pyrrole.²²⁴ However, the activity of the heterogeneous catalyst decreased after the second cycle.

Acknowledgments

Financial support from the *Ministerio de Educación y Ciencia* of Spain (Projects CTQ2005-04968-C02-01, CTQ2006-04204), *Consolider Ingenio* 2010 (Project CSD2007-00006), and Generalitat de Catalunya (Project SGR2005-00305) is gratefully acknowledged.

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