

Nanoparticles as Recyclable Catalysts: The Frontier between Homogeneous and Heterogeneous Catalysis

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Keywords:

C–C coupling · dendrimers · gold · nanoparticles · palladium · supported catalysts



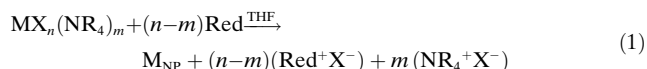
Interest in catalysis by metal nanoparticles (NPs) is increasing dramatically, as reflected by the large number of publications in the last five years. This field, “semi-heterogeneous catalysis”, is at the frontier between homogeneous and heterogeneous catalysis, and progress has been made in the efficiency and selectivity of reactions and recovery and recyclability of the catalytic materials. Usually NP catalysts are prepared from a metal salt, a reducing agent, and a stabilizer and are supported on an oxide, charcoal, or a zeolite. Besides the polymers and oxides that used to be employed as standard, innovative stabilizers, media, and supports have appeared, such as dendrimers, specific ligands, ionic liquids, surfactants, membranes, carbon nanotubes, and a variety of oxides. Ligand-free procedures have provided remarkable results with extremely low metal loading. The Review presents the recent developments and the use of NP catalysis in organic synthesis, for example, in hydrogenation and C–C coupling reactions, and the heterogeneous oxidation of CO on gold NPs.

1. Introduction

In a recent “Focus” Article in *Chemical Communications*, Somorjai emphasized that catalysis is the central field of nanoscience and nanotechnology,^[1a] and finds parallels between enzyme catalysis and heterogeneous catalysis, even though this idea in reality remains a dream. As admitted by Somorjai, selectivity is still a major problem in heterogeneous catalysis that involves the top-down approach, even though up-to-date techniques, such as size-reduction lithography, permit access to nanocatalysts.^[1] On the other side of the catalysis world, mononuclear transition-metal complexes have recently achieved an amazing level of performance in terms of selectivity,^[2] just think of the amazing progress in C–C coupling^[2a–c] and metathesis^[2d] reactions. The ultimate goals of recoverable catalysts, their criteria of evaluation, and their role in “Green Chemistry” have been emphasized in recent articles.^[3]

Many important homogeneous catalysts are used in industry in biphasic systems or by fixation on supports, the bridge between these two approaches is now being built through the use of nanoparticles (NPs; sometimes called giant clusters, nanoclusters, or colloids) whose activity is very high under mild conditions because of their very large surface area.^[4–11] This frontier domain is sometimes called “semi-heterogeneous”. Contrary to classic heterogeneous catalysts,^[1] these NPs are synthesized by the bottom-up approach from molecular precursors including a metal salt, a molecular stabilizer, and a reducing agent (a typical preparation is given in Equation (1); M = Metal from Group 8–10, X = Cl or Br, R = C_{4–12} alkyl, Red = M'H with M' = H, Li, LiBEt₃, NaBEt₃, KBEt₃).^[4–7,11] Physical means of preparation,^[6–8,10,11] such as

the electrochemical route developed by Reetz,^[7] are also numerous.^[4,5,7,11]



Another modern synthesis, inspired by the 150-year old method of Faraday^[8a,b] and popularized by Schiffrin's group in 1993,^[8a,c] involves reduction by NaBH₄ of a metal precursor such as HAuCl₄^[8a,c] or Na₂PdCl₄^[8d] in a biphasic organic-solvent–water system in the presence of the phase-transfer reagent [N(C₈H₁₇)₄]Br and subsequent addition of a stabilizer such as a thiol for AuNPs and (4-dimethylamino)pyridine in the case of PdNPs. NPs can be soluble and thus act homogeneously (soluble AuNPs were discovered over 2500 years ago and were used for aesthetic and curative purposes).^[8a] The stabilization of NPs during their synthesis can be by electrostatic, steric, electrosteric (a combination of steric and electrostatic, see Figure 1) means or through the use of ligands.^[4,5,8,11] M⁰NP synthesis can also be carried out by the vaporization of the atomic metal or of M⁰ complexes.^[11] In view of the catalyst recycling, NP catalysts often are immobilized or grafted on inorganic or organic polymer supports.^[4,5,8,11] There are many reviews on the numerous synthetic routes for NPs,^[4–11] and herein in we will not cover

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this aspect in detail. We will rather focus on catalysis with emphasis on the most recent work, after a brief survey of the background. For this Review, we will classify and discuss the categories of NP catalysts by the type of support.

2. Pioneering Studies

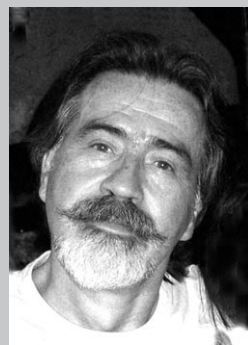
The use of NPs in catalysis appeared in the 19th century with photography (AgNPs) and the decomposition of hydrogen peroxide (PtNPs).^[5d] Pioneering catalytic applications of NPs were reported in 1940 by Nord on nitrobenzene reduction,^[9a] in 1970 by Parravano on hydrogen-atom transfer between benzene and cyclohexane and oxygen-atom transfer between CO and CO₂ using AuNPs.^[9b] The real breakthrough came with Haruta's seminal studies on oxide-supported AuNP-catalyzed CO oxidation by O₂ at low temperatures.^[9c-e] In the 1970s, Bond and Sermon^[9f] and Hirai et al.^[9g] disclosed AuNP-catalyzed olefin hydrogenation. In 1986 Lewis demonstrated the colloidal mechanism for the catalysis of olefin



Didier Astruc, born in Versailles, 1946, obtained his PhD in Rennes with Prof. R. Dabard (ferrocenes-cages) and was a NATO post-doctoral fellow at MIT with Prof. R. R. Schrock. He has been a Senior Member of l'Institut Universitaire de France since 1995, a Member of the French CNRS committee since 2000, and the President of the Coordination Chemistry Division of Société Chimique de France since January 2002. He was awarded numerous prizes including the 1989 Humboldt Prize and the 2000 Le Bel Prize. His research interests are now mainly focused on metallodendrimers and nanoparticles.



Feng Lu obtained his PhD under the supervision of Prof. C. Elschenbroich in Marburg in 2002, then joined Professor Didier Astruc at University Bordeaux I with where he worked for a year on nanoparticle catalysis. He is presently a post-doc with Professor Christopher B. Gorman in North Carolina State University at Raleigh working on metallodendrimers. His research interests cover biocatalysts, biosynthesis, dendrimers, electron transfer, molecular electronics, organometallic chemistry, and solar energy conversion.



Jaime Ruiz Aranzaes studied at the Catholic University Santiago (Chile) where he passed his Master degree in chemistry with Professor E. Roman, then moved to Bordeaux to prepare a PhD on the kinetics of substitution reactions of 19-electron complexes with Professor Didier Astruc and then his Habilitation on polyaromatic-iron chemistry. He is presently guiding a research group in the same laboratory, his interests being in the area of the synthesis, chemistry, electrochemistry, and physical properties of redox-active nano-organometallics.

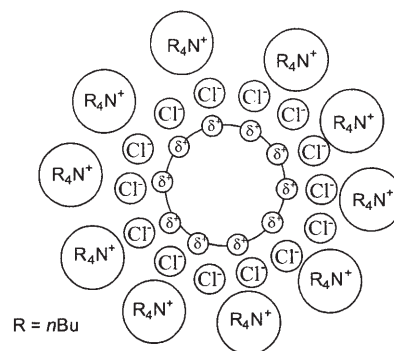


Figure 1. “Electrosteric” (that is electrostatic and steric) stabilization of metal nanoparticles obtained by reduction of a metal chloride salt in the presence of a tetra-*N*-alkylammonium cations. The halide anions provide electrostatic stabilization, and the tetrabutylammonium cations steric stabilization) (Bönnemann-type synthesis based on Equation (1)). The presence of chloride or other anions (and not the ammonium cations) at the nanoparticle surface was demonstrated. Anions stabilized IrNPs in the following order: polyoxometallate > citrate > polyacrylate \approx chloride. Thus, the stabilization of metal NPs by anions can also have an important steric component.^[25f,g]

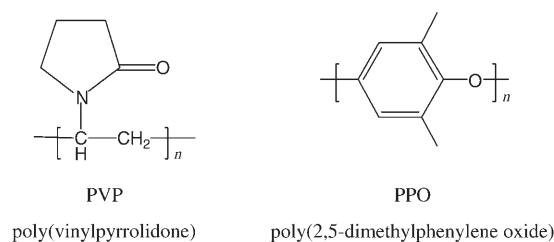
hydrosilylation by silanes using organometallic complexes of Co, Ni, Pd, or Pt including the Speier catalyst (alcoholic H₂PtCl₆).^[9h] These catalysts were formerly believed to follow the classic monometallic organometallic mechanism (oxidative addition of the Si–H bond of the silane onto the transition-metal center and subsequent alkene insertion and reductive elimination). That decade saw the beginning of extended NP catalytic studies especially in the fields of redox catalysis, photocatalysis (photocatalytic water splitting and photo-hydrogenation of alkenes, alkynes, and CO₂),^[10a-g] hydrogenation of unsaturated substrates, and oxidation.^[10h,i] In the mid-1990s, pioneering studies of PdNP catalysis were reported by Reetz for Heck C–C coupling, such as the reaction between butyl acrylate and iodobenzene or aryl bromides and styrene.^[7]

The first years of the 21st century have seen an exponential growth in the number of publications in the NP field. The main goals are 1) improving catalyst activities and selectivities and 2) understanding the catalytic mechanisms.^[11] The modes of preparation of catalytically active NPs have been diversified and currently include impregnation,^[12a] co-precipitation,^[12a,b] deposition/precipitation,^[12c] sol-gel,^[12a,d] gas-phase organometallic deposition,^[12f] sonochemical,^[12g] micro-emulsion,^[12h] laser ablation,^[12i] electrochemical,^[12j] and cross-linking.^[12k]

3. Stabilizers for Metal Nanoparticles

3.1. Polymers

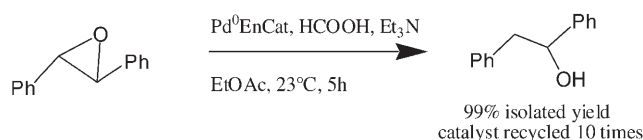
Polymers provide stabilization for metal NPs through the steric bulk of their framework, but also by binding weakly to the NP surface through heteroatom that play the role of ligands. Poly(*N*-vinyl-2-pyrrolidone) (PVP) is the most used polymer for NP stabilization and catalysis, because it fulfill both steric and ligand requirements (Scheme 1).^[5f] PVP-



Scheme 1. Two major polymer families used as metal NP supports for catalysis.

stabilized Pt-, Pd-, and RhNPs, that are synthesized by the reduction of the corresponding metal halide in refluxing ethanol and immobilized in an ionic liquid, 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([BMI][PF₆]), are very efficient olefin and benzene hydrogenation catalysts at 40 °C that can be recycled without loss of activity.^[12k]

Using standard PVP-stabilized NP catalysts, parameters such as size and stability during the catalytic process have been examined. For instance, decreasing the PdNP size down to 3 nm in the Suzuki reaction improved the catalytic activity, suggesting that the low-coordination-number vertex and edge atoms on the particle surface are the active catalytic sites.^[13] Many other polymers have recently been used as efficient supports for NP catalysis: polyurea (Scheme 2),^[14a] polyac-



Scheme 2. Ring-opening hydrogenolysis of epoxides catalyzed by PdNPs (2 nm) microencapsulated in polyurea. The system can be recycled at least ten times with 97–99% yield.^[14a]

rylonitrile and/or polyacrylic acid (Figure 2),^[14b] multilayer polyelectrolyte films (Figure 3),^[14c] polysilane micelles with cross-linked shells (Scheme 3),^[14d] polysiloxanes (Scheme 4),^[14e] oligosaccharides,^[14f] copolymers synthesized by aqueous reversible addition–fragmentation chain-transfer polymerization,^[14g] π -conjugated conducting polypyrroles,^[14h] poly(4-vinylpyridine),^[14i] poly(*N,N*-dialkylcarbodiimide),^[14j] polyethylene glycol,^[14k] chitosan^[14k] and hyperbranched aromatic polyamides (aramids).^[14l] Classic surfactants such as sodium dodecylsulfate (SDS) are also used as NP stabilizers for catalysis.^[14m] Water-soluble polymers have been used with success for selective hydrogenation of cyclic versus noncyclic olefins.^[5d]

A very important concept pioneered in the 1970s is that of catalysis using two different metals such as Au and Pd in the same NP.^[15] This idea has been beautifully developed by Toshima's group who used PVP to stabilize core–shell bimetallic Au–PdNPs, that is, NPs in which the core is Au and the shell is Pd (Figure 4).^[16] After co-reduction, the structure is controlled by the order of reduction potentials of both ions and coordination abilities of both atoms to PVP. The location of Au in the core and Pd on the shell was

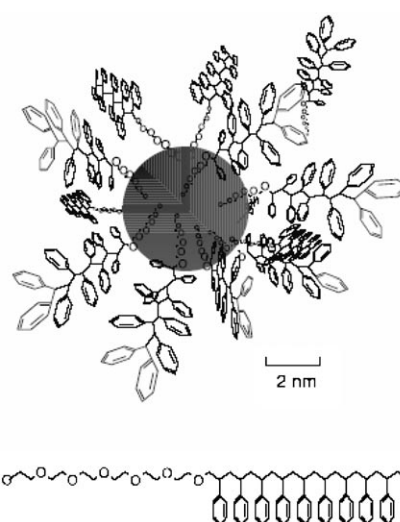


Figure 2. PdNP adsorbed on polyacrylic acid block copolymer as hydrogenation catalyst: the PdNP is stabilized through the block copolymer. Reprinted with permission from ref. [14c].

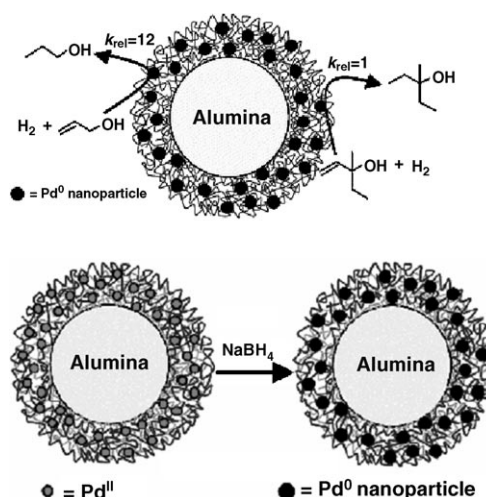
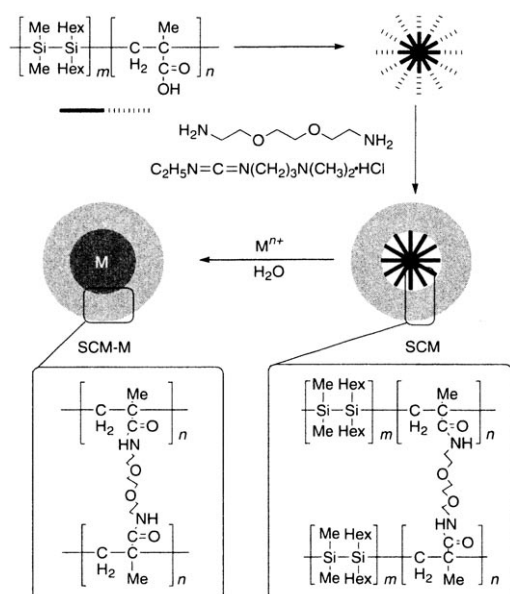


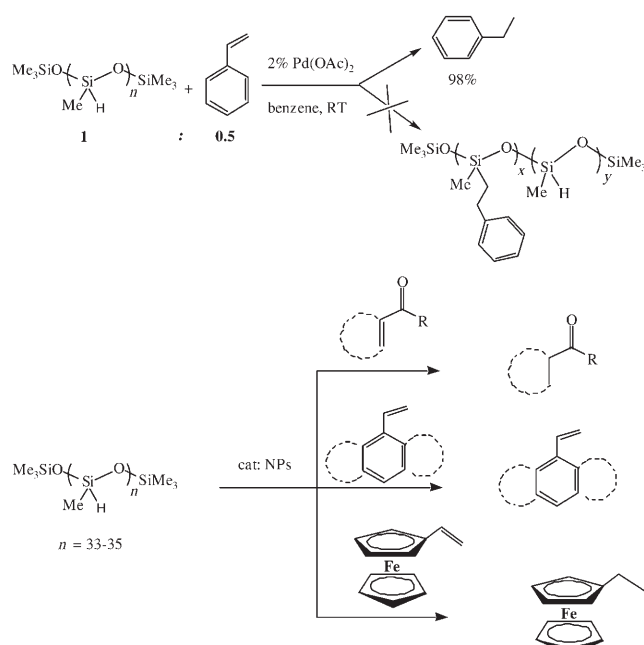
Figure 3. Principle of the formation of PdNPs in multilayer polyelectrolyte films for selective hydrogenation (the layer-by-layer deposition is both convenient and versatile). Reprinted with permission from ref. [14d].

demonstrated by extended X-ray absorption fine structure spectroscopy (EXAFS), and it was shown that such heterobimetallic Au-cored PdNPs are more active in catalysis than simple PVP-stabilized PdNPs. Thus, the Au core enhances the catalytic properties of PdNPs at the PdNP surface.^[5f,g] Conversely, design strategies can lead to the opposite core–shell structure (Pd core, Au shell), and specific catalytic properties were obtained for methylacrylate hydrogenation.^[16]

Cyclohexene hydrogenation was catalyzed with PdNPs stabilized by highly branched amphiphilic polyglycerol (75% esterified with palmitoyl chloride) and this system was used in a continuously operating membrane reactor to enable recovery and recycling of the PdNP catalyst.^[16c]



Scheme 3. Schematic illustration of the synthesis of metal NPs derived from polysilane-shell cross-linked micelle templates (Reprinted with permission from ref. [14f]).



Scheme 4. Polysiloxane-supported PdNPs, generated by reduction of $\text{Pd}(\text{OAc})_2$ with polymethylhydrosiloxane, as recyclable chemoselective hydrogenation catalysts. Top: selective reduction of styrene, bottom: reduction of alkenes.^[14e]

3.2. Dendrimers

Dendrimers, like polymers, are macromolecules; but unlike polymers, there are perfectly defined on the molecular level with a polydispersity of 1.0.^[17] Having shapes that resemble molecular trees or cauliflowers, they become globular after a few generations, and thus behave as

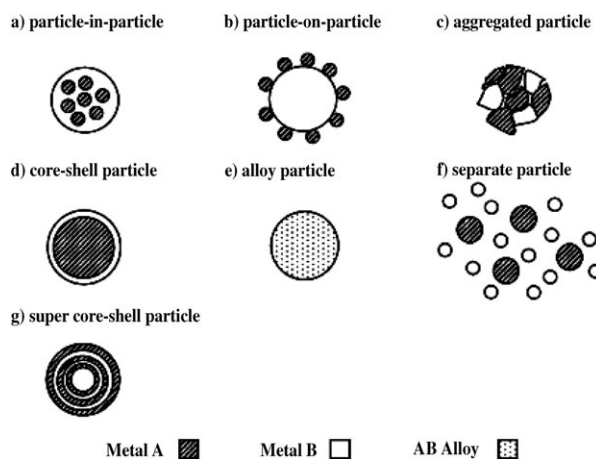


Figure 4. Representative morphologies of bimetallic nanoparticles. Reprinted with permission from ref. [16a].

molecular boxes^[17c] that can entrap and stabilize metal NPs especially if there are heteroatoms in the dendrimer's interiors.^[17d,18] The dendritic branches and termini can serve as gates to control the access of small substrates into the dendrimer and thus to the encapsulated NP. Finally, the dendrimer terminal groups can be chosen to provide the desired solubility in organic, aqueous, or fluoruous medium. The formation of NPs stabilized by dendrimers for catalysis has been proposed in 1998 by the three research groups of Crooks,^[18] Tomalia^[19a,b] and Esumi.^[19c-e] Metal NPs were introduced inside the dendrimers,^[18,19a,b] or at the dendrimer periphery.^[19c-e] The former strategy has proved very successful because of the molecular definition of dendrimers and their ability to serve as a box and generation-dependent filter of substrates.

Crooks and co-workers complexed metal ions (Cu^{2+} , Au^{3+} , Pt^{2+} , Pd^{2+} , Fe^{3+} , Ru^{3+}) to the inner nitrogen atoms of the tertiary amines of poly(amidoamine) (PAMAM) dendrimers. The reduction of the metal ions to M^0 by NaBH_4 provoked the agglomeration of the metal atoms to NPs inside the dendrimer.^[18] When the terminal amino groups were protonated at pH 2 prior to complexation by metal ions, the metal ions proceeded selectively onto the inner nitrogen atoms resulting in water solubility of the dendrimer and subsequent catalytic activity in water. For example, the selective hydrogenation of allylic alcohol and *N*-isopropyl acrylamide was catalyzed in water by such PAMAM dendrimer–PdNPs (Figure 5 and Scheme 5). Terminal amino groups can be converted into amide groups by the addition of decanoic acid so that the dendrimer–NP catalyst becomes soluble in toluene. In this solvent the catalyst hydrogenates the substrates more rapidly than in water. Alternatively, a perfluorinated polyether “ponytail” can be covalently grafted to the PAMAM dendrimer PdNP catalyst making it soluble in supercritical CO_2 . This catalyst was shown to perform classic palladium-catalyzed Heck coupling between aryl halides and methacrylate yielding predominantly (97%) *trans*-cinnamaldehyde. Oxidation^[18] and reduction^[20] catalysis could also be performed using such dendrimer-encapsulated NPs.

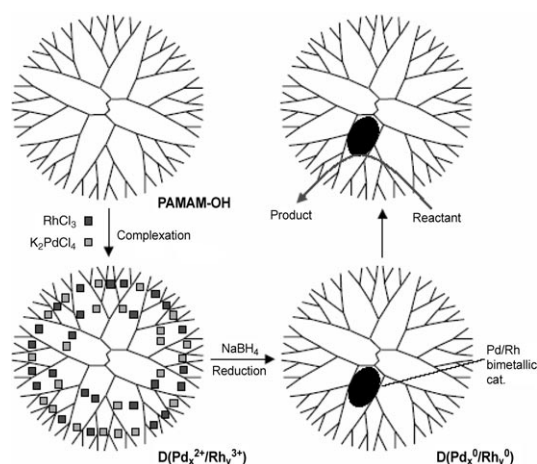
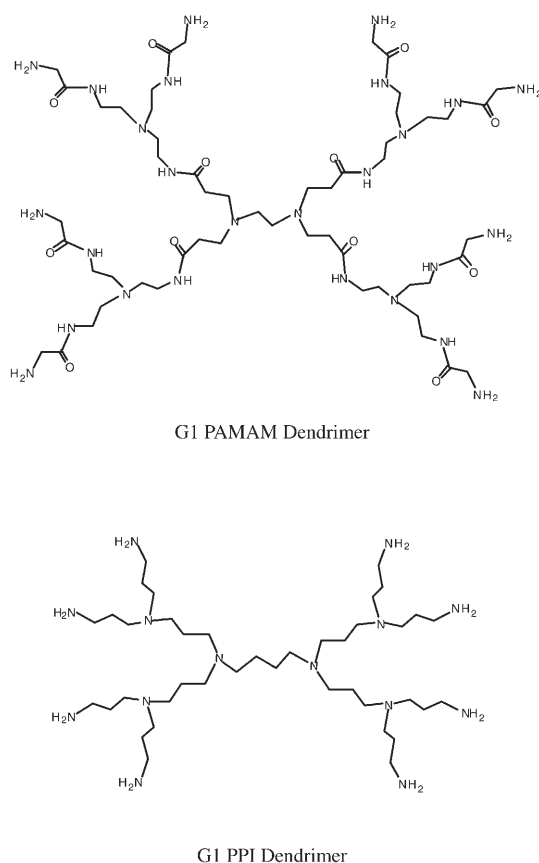


Figure 5. Strategy pioneered by Crooks for the catalysis by nanoparticles encapsulated in PAMAM or PPI dendrimers: complexation of a metal cation to the inner nitrogen atoms of tertiary amines, then reduction to metal(0) by NaBH_4 , and aggregation giving the NPs inside the dendrimer. The use of PPI dendrimers requires control of the pH value before metal ion complexation to ensure protonation of the terminal amino groups ($\text{p}K_a = 9.5$), not the inner ones ($\text{p}K_a = 5.5$). In the PAMAM series, OH-terminated dendrimers are used.^[18f] Specifically, the preparation of dendrimer-encapsulated bimetallic NPs is shown. Reprinted with permission from ref. [23].



Scheme 5. The two families of commercial dendrimers considered as metal nanoparticle supports for catalysis (only the first generation (G1) is represented). PPI dendrimers are smaller than PAMAM (2.8 nm versus 4.5 nm for G4, respectively), but more stable (470 °C versus 100 °C respectively).^[11b]

El Sayed and co-workers investigated the effect of the generation of the PAMAM dendrimer on the catalytic activity in the Suzuki C–C coupling reaction between phenyl iodide and phenylboronic acid at 80 °C.^[21] Generations 3 and 4 were found to be good stabilizers (in contrast to generation 2). These dendrimers stabilize the metal NPs by preventing their agglomeration, but they do not fully passivate the metal surface. The PAMAM-dendrimer-stabilized PdNPs (1.3 ± 0.1 nm) were compared to PVP-stabilized PdNPs (2.1 ± 0.1 nm) for this Suzuki reaction carried out in MeCN:H₂O 3:1 at 100 °C. The mechanism was found to be similar in both cases with phenylboronic acid adsorption onto the NPs, but the turnover ratio for the 2nd cycle:1st cycle was higher for the dendrimer-PdNP catalyst.

Using a different mode of synthesis, 4th-generation (G4) PAMAM-dendrimer-stabilized PdNPs (3.2 ± 1 nm) were prepared by Christensen and co-workers.^[22a] With this catalytic system Suzuki coupling occurs with iodobenzene in EtOH at 78 °C, whereas bromobenzene requires a temperature of 153 °C in DMF.^[22a] The amount of catalyst was only 0.055 %, which is significantly smaller than traditional catalysts. It was suggested that, since the G4-dendrimer diameter is only 4.5 nm, the PdNPs are stabilized, rather than encapsulated, by the dendrimer.

In studies with 3rd to 5th-generation poly(propyleneimine) (PPI) dendrimers that were functionalized by reaction with triethoxybenzoic acid chloride, the dendrimer-stabilized PdNP catalyst led to substrate specificity for the hydrogenation of polar olefins, owing to the strong interaction between polar substrates and the inner tertiary amino groups.^[22b,c] For example, in competitive hydrogenation reactions of 3-cyclohexene-1-methanol and cyclohexene, G5-PdNPs gave only reduction of the 3-cyclohexene-1-methanol whereas the traditional Pd/C catalyst gave incomplete hydrogenation of both compounds under the same conditions (Figure 6). For third-generation PdNP-cored dendrimers catalytic activity has been found for the Heck reaction of iodobenzene with ethylacrylate in refluxing toluene (75 % yield) and Suzuki reactions of iodo- and bromobenzene with $\text{PhB}(\text{OH})_2$ in refluxing ethanol (42–47 % yield) have been observed. No activity was obtained for hydrogenation reactions, however.^[22d]

The encapsulation strategy has recently been extended to bimetallic NP catalysts,^[23] evidence that these NPs are bimetallic being provided by single-particle X-ray dispersive spectroscopy (EDS).^[17a,b] It was shown that the G4-PAMAM Pd–MNPs (M = Pt or Au) more efficiently catalyze allylic alcohol hydrogenation than the analogous monometallic Pt or Pd catalyst or a mixture of both (Scheme 6).^[18i,k]

When a PdNP was located at the dendritic core of G3-TEBA dendrimer, Heck and Suzuki coupling could be obtained in 38 % to 90 % yield in refluxing toluene or ethanol for a day. The form of NPs within the dendrimer is not clear despite TEM studies. Are the NPs really completely inside the dendrimer? Is the dendritic core encapsulated in the NP? Are there several close NPs in the dendrimer cavities or are they connected? Likewise, more work is called for in order to understand the very nature of the catalytically active Pd species.

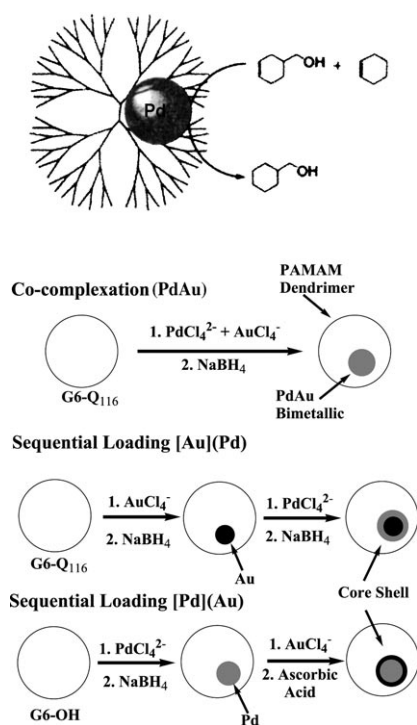
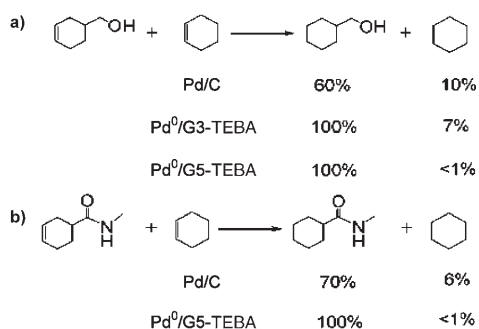


Figure 6. Modes of synthesis of PAMAM-dendrimer-encapsulated heterobimetallic Pd–AuNPs. Reprinted with permission from ref. [18k].



Scheme 6. Competitive hydrogenation of a) 3-cyclohexene-1-methanol and cyclohexene b) *N*-methyl-3-cyclohexene-1-carboxamide and cyclohexene using various palladium catalysts. TEBA = triethoxybenzamide-terminated poly(propylene imine) dendrimer. Reprinted with permission from ref. [22b].

A different dendrimer-stabilizing strategy involves coordination of the NPs by the surface amino groups of PAMAM and PPI dendrimers,^[19c–e] and these catalysts were used for various catalytic reactions including the reduction of 4-nitrophenol. In this case, the PdNPs may be surrounded by a number of dendrimers that can also bridge the nanoparticles.

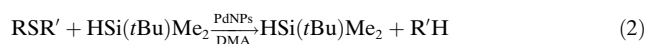
In both situations, the dendrimers clearly stabilize small nanoparticles by a combination of polyligand and steric effects. Whether these dendrimer-stabilized PdNPs are the active species in palladium-catalysis or reservoirs of much smaller, very active palladium fragments, is unclear.

3.3. Ligands

The introduction of ligands as NP stabilizers is of special interest, because it focuses on the precise molecular definition of the catalytic materials. This strategy potentially allows optimization of the parameters that govern the efficiency in catalytic reactions, including enantioselective ones.

Gladysz showed that thermomorphous fluororous palladacycles act as PdNP catalyst precursors for the Heck reaction at 80–140 °C in DMF and gave very high turnover numbers.^[24a] Molecular palladium complexes, such as palladacycles and other palladium salts, were also used as PdNP precursors. Treatment with CO in DMF or toluene at room temperature gave PdNPs that catalyzed nucleophilic substitution/carbonylation/amination affording *iso*-indolinones at room temperature.^[24b] PdNPs capped with special ligands such as polyoxometallates^[25] and cyclodextrins^[26] were shown to be active for the catalysis of the hydrogenation of unsaturated substrates and for the Suzuki, Heck, and Stille reactions. For example, perthiolated β -cyclodextrin-PdNPs (1%), in the presence of K₂CO₃ or Ba(OH)₂, catalyze the coupling of iodo- and bromoarenes and iodoferrocene to phenyl boronic acid in refluxing in MeCN:H₂O, 1:1 (v/v).^[26a] These 3 nm PdNPs are also active for the hydrogenation of water-soluble alkenes.^[26b,c] The simplest dodecathiolate-PdNPs catalyze the Suzuki reaction of haloarenes including chloroarenes with phenylboronic acid even at ambient temperature, and the catalyst can be recycled several times.^[27]

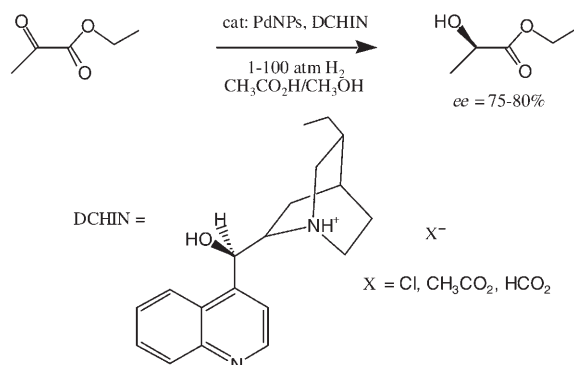
Another very simple mode of stabilization involves addition of silanes R₃SiH, such as *tert*-butyldimethylsilane, to PdX₂ (X = Cl[−], OAc[−]) in *N,N*-dimethylacetamide. The black NP solution formed in this way catalyzes silane alcoholysis of sugars^[28a] and selective cross-coupling of the silane with phenyl and vinyl thioethers giving the corresponding thio-silanes and silthianes [Eq. (2); R and R' = alkyl, aryl; DMA = *N,N*-dimethylacetamide; T = 25 °C].^[28b]



The synthesis of core–shell NPs that have a cheap-metal core, such as nickel, and a noble metal shell, such as palladium, has been achieved by the thermal decomposition (235 °C) of the Pd and Ni precursors ([Ni(acac)₂] + [Pd(acac)₂] + trioctylphosphine; acac = 2,4-pentanedione), the nickel complex decomposes before the palladium one. The nickel-cored PdNPs show a much better activity than PdNPs without nickel, but with the same amount of Pd atoms, for the Sonogashira coupling of *p*-bromoacetophenone with phenylacetylene in toluene at 80 °C, although *p*-chloroacetophenone was unreactive.^[28c]

Enantioselective reactions have been carried out with metal NPs.^[29–30] The first example of an asymmetric reaction catalyzed by metal NPs was reported by the group of Lemaire, Besson, and Galez in 1994 for the RhNP-catalyzed hydrogenation of 2-methylanisole *o*-cresol trimethylsilyl ether induced by a RhNP with a chiral amine, *R*-diocetylhexyl-1-ethylamine, as ligand.^[29] The hydrogenation of ethyl pyruvate was found by Bönemann and co-workers^[30a] to be efficiently catalyzed by Pt- or PdNPs with cinchonidine

ligands (75–80% *ee*, Scheme 7). The *ee* value was later improved (up to 95–98%).^[30b-d] Fujihara and co-workers reported 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (binap)—stabilized PdNPs with a diameter of 2.0 ± 0.5 nm



Scheme 7. Enantioselective hydrogenation of ethyl pyruvate catalyzed by cinchonidine-PtNP or cinchonidine-PdNPs.^[30a]

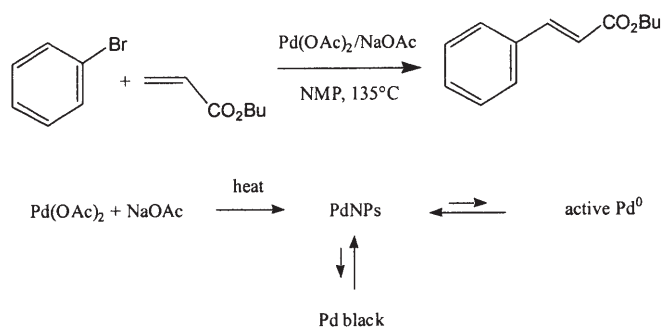
and narrow size distribution. It was found that these binap-PdNPs catalyze the asymmetric hydrosilylation of styrene under mild conditions (*ee* 95% at 0°C), whereas mononuclear binap-Pd complexes are inactive.^[30e] Recently, the Gomez and Chaudret groups reported enantioselective allylic alkylation reactions with 97% *ee* that were catalyzed by PdNPs stabilized by a chiral xylofuranide diphosphite.^[30f] In the above mentioned reports it is suggested that the nanoparticles themselves are catalytically active. However, the nature of the catalytically active species (and even whether catalysis actually occurs on the NP surface) remains unclear. The catalytically active species could also be much smaller Pd fragments, that are leached from the NP, and to which the asymmetric ligand is bound. In any case, regardless of the mechanism, the selectivity obtained is remarkable.

3.4. “Ligand-free” Heck Reactions Using Low Palladium Loading and the Resulting Mechanistic Implications

The original work by Mizoroki et al.^[31a] then by Heck et al.^[31b] on the palladium-catalyzed coupling reaction of aryl iodides with olefin used a palladium salt (PdCl_2 and $\text{Pd}(\text{OAc})_2$, respectively), a base (NaOAc and NBu_3 , respectively) and a solvent (methanol and *N*-methylpyrrolidone, respectively), but no phosphine or other ligand. Beletskaya and co-workers reported a similar phosphine-free reaction of iodo- and bromoarenes in water, and the palladium loading was as low as 0.0005 mol % (for which the term “homeopathic dose” was used) in the case of 3-iodobenzoic acid.^[31c] Likewise, the Reetz^[31d,n] and de Vries^[31e,n] groups reported extremely efficient Heck catalysis with similarly low palladium-loadings for the coupling between aryl bromides and styrene in organic solvents. Reetz also found that PdNPs are formed when PdCl_2 , $\text{Pd}(\text{OAc})_2$, or $\text{Pd}(\text{NO}_3)_2$ is warmed in THF in the presence of a tetrabutyl ammonium carboxylate that functions as a reducing and stabilizing agent.^[31f] Heating

$\text{Pd}(\text{OAc})_2$ in polar solvents such as propylene carbonate also generated PdNPs. PdNPs generated in this way from $\text{Pd}(\text{OAc})_2$ ^[31d-f] or palladacycles^[31g-i] are active catalysts in the Heck reaction, this was demonstrated by monitoring the reactions using TEM.^[31j]

Very interestingly, it was found that the palladium catalyst “improves” upon lowering the palladium loading. The proposal to account for this observation was an equilibrium between small (monomeric or dimeric) catalytically active palladium species and the PdNPs which serve as a catalyst reservoir.^[31d,h,k] When the catalyst concentration is too high, inactive palladium black forms (Scheme 8). This result



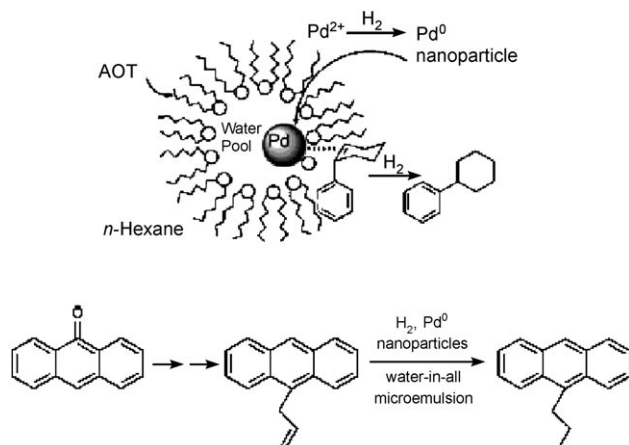
Scheme 8. Heck-type reactions catalyzed by extremely low loadings of palladium salts.^[31d,f,i,n]

indicates that the rate of the catalytic reaction must be extremely high, since most of the palladium is in the form of PdNPs. This type of Heck reaction seems quite general for aryl bromides and has been scaled up by the firm DSM to kilogram scale to prepare a drug intermediate.^[31e] Likewise, a range of enantiopure substituted *N*-acetylphenylalanines were obtained from methyl *N*-acetamido acrylate and various bromoarenes at very low palladium loading in the absence of other ligands, followed by rhodium-catalyzed hydrogenation.^[31i] De Vries reported a similar behavior for the Suzuki reaction of aryl bromides with a turnover frequency (TOF) of up to 30 000 mole of product per mole of catalyst per hour.^[31m] The precise nature of the active species in these palladium-catalyzed C–C coupling reactions is not known, and it may well be an monomeric- or dimeric Pd^0 species to which an anionic ligand (Cl^- or OAc^-) is bound. This type of reaction is very important in terms of “Green Chemistry” as in it waste is minimized through the absence of added ligand and by such low palladium loadings.^[31n] This concept could be extended to other types of catalysis, and indeed other examples of NP catalysts are known for platinum-catalyzed hydrosilylation^[5c] and ruthenium-catalyzed hydrogenation.^[31o-q] RuNPs have also been shown to catalyze the Heck reaction.^[31r]

3.5. Micelles, Microemulsions and Surfactants

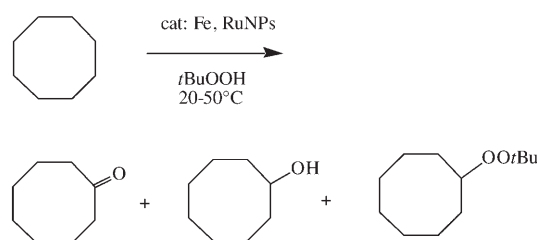
“Fluorous” strategies^[32] have been used on various occasions for NP catalysis for instance by the Crooks^[17] and Gladysz^[3,24a] groups. Fluoro surfactants can also serve as micellar stabilizers for PdNPs in water-in-supercritical CO_2

(scCO₂) microemulsions. Such systems were used as hydrogenation catalysts for simple olefins^[32b-d] and citral.^[32e] In these systems, hydrogen can work both as a reducing agent for palladium salts and for the unsaturated substrate. Ultrafine PdNPs in reverse micelles (KBH₄ used to reduce the Pd^{II} precursors) enabled the catalytic hydrogenation of allylic alcohol and styrene in the solvent isooctane, although the bis(2-ethylhexyl) sulfosuccinate surfactant inhibited the hydrogenation activity (Scheme 9).^[32f] The oxidation of



Scheme 9. Hydrogenation of 10-(3-propenyl) anthracene catalyzed by PdNPs in water-in-oil microemulsion (the reaction is much faster than with Pd/C catalysts). AOT = sodium-5-14-diethyl-8,11-dioxo-7,12-dioxo-octadecane-2-sulfonate. Reprinted with permission from ref. [32f].

N,N,N',N'-tetramethyl-*p*-phenylenediamine by [Co(NH₃)₅Cl]²⁺ was catalyzed by PdNPs in an aqueous/AOT/*n*-heptane microemulsion.^[32g] Functional olefins such as 4-methoxycinnamic acid were selectively hydrogenated in scCO₂ using PdNPs in a water-in-scCO₂ microemulsion, as was nitrobenzene (to aniline).^[32h] Oxidation of cyclooctane by *tert*-butylhydroperoxide (*t*BHP) was catalyzed by FeNPs in reverse microemulsion or with RuNPs in biphasic water/cyclooctane solvent. The catalyst could be recycled without loss of activity (Scheme 10).



Scheme 10. Cyclooctane oxidation catalyzed by FeNPs in reverse microemulsions or by RuNPs in biphasic water-organic media.^[49]

4. Ionic liquids as Media for Metal-Nanoparticle Catalysis

Ionic liquids (ILs) are valuable media for catalysis with PdNPs. The substituted imidazolium cation is bulky, favoring

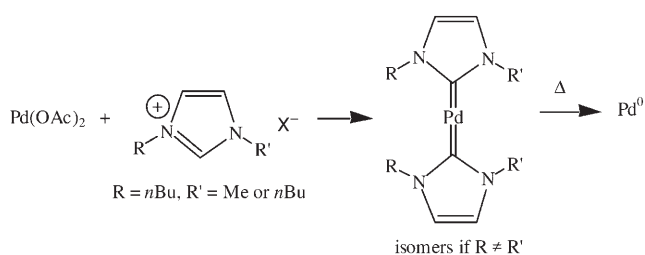
the electrostatic stabilization of NPs (as do *t*Bu₄N⁺ ions in Figure 1). The size of the imidazolium cation (that can eventually be tuned by the choice of the *N*-alkyl substituents) also has an important influence on the stabilization, size, and solubility of the NPs, factors which play a role in catalysis. However, ILs are non-innocent, at high temperatures they readily produce palladium-*N*-heterocyclic carbene complexes from PdNPs upon deprotonation of the imidazolium salt. Thus, these carbene ligands can be bound to the NP surface or form mononuclear mono- or biscarbene complexes with palladium atoms that have been leached from the PdNP surface.^[33]

IrNPs in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) were used directly for the hydrogenation of olefins, and good results were obtained.^[33b] Phenanthroline (phen) stabilized PdNPs prepared in [BMIM][PF₆] according to the method reported by Schmid and co-workers^[33c] (but without using acetic acid as the solvent: Pd(OAc)₂ + Phen-H₂O + 1 atm H₂ in the IL at room temperature), efficiently catalyzed the hydrogenation of olefins and the selective hydrogenation of cyclohexadiene to cyclohexene under mild conditions (1 atm H₂, 40 °C). Under these conditions, formation of palladium carbene complexes from the BMIM ions does not occur, thus the IL simply plays the role of a PdNP-stabilizing solvent. This catalyst could be reused several times,^[33d] and it was much more active than phenanthroline-protected PdNPs supported on TiO₂ for the hydrogenation of 1-hexene.^[6b] It was found that PdNPs, formed by reaction of Pd(OAc)₂ with tetrabutylammonium acetate dissolved in tetrabutylammonium bromide, efficiently catalyzed the stereospecific reaction of cinnamates with aryl halides to give β-aryl-substituted cinnamic esters.

As indicating in the beginning of this section, the role of the IL is crucial in both the PdNP formation and for the stereospecificity of C–C coupling that could not be obtained in previous studies of PdNP-catalyzed Heck reactions.^[33e-g] Salts of *N*-butyronitrile pyridinium cation react with PdCl₂ to give dinitrile complexes that turn black upon addition of phenyl-tributylstannane, and the PdNPs formed catalyze Stille and Suzuki C–C coupling reactions. It is believed that the nitrile groups coordinate to the PdNP surface, which results in PdNP stabilization.^[33h]

PdNPs are formed from palladium acetate in the presence of 1,3-dibutylimidazolium salts. It was suggested that *N*-heterocyclic palladium carbene complexes are generated which form the PdNPs that catalyze Suzuki coupling.^[33i] Such carbene complexes were shown to form and catalyze the Heck reaction, and it is strongly suspected that the catalytically active species are in fact PdNPs which form under these conditions.^[33e-j] Indeed, heating these *N*-heterocyclic palladium carbene complexes lead to PdNP formation after ligand loss (Scheme 11). The selectivity of the reactions in such IL media also depends on the solubility, and the solubility difference can be used for the extraction of the product.^[33k-m]

Ionic liquids are favorable media for the electrostatic stabilization of preformed NPs at room temperature and subsequent catalysis. At high temperature they give palladium-carbene complexes upon deprotonation of the imida-



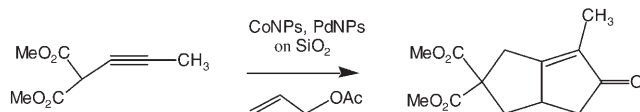
Scheme 11. Formation of palladium carbene complexes by the reaction between palladium acetate and imidazolium salts. Subsequent decomposition at high temperature gives catalytically active PdNPs for Heck-type reactions.^[33e,i,j]

zolium cation, these carbene complexes in turn generate, PdNP catalysts.

5. Solid Supports for Metal Nanoparticles

5.1. Oxide supports

A large number of recent reports (for earlier reports, see refs [6] and [11]) focus on the catalytic properties of NPs supported on metal oxides, including oxides of Si,^[34,35] Al,^[36] Ti,^[37] Zr,^[43] Ca,^[38] Mg,^[39,43] and Zn.^[39g] These oxides take various forms, such as SiO₂ aerogels or sol-gels such as Gomasil G-200, high-surface silica (for example, see Scheme 12), M41S silicates and aluminosilicates, MCM-41



Scheme 12. Sequential allylic alkylation and Pauson–Khand reactions for the one-pot syntheses of bicyclic enones. Both are catalyzed by CoNPs and PdNPs supported on silica.^[35c]

mesoporous silicates such as HMS and SBA-15 silica, silica spheres,^[35b] microemulsions (SiO₂), hydroxyapatite (Ca²⁺),^[38] hydrotalcite (Mg²⁺, Al³⁺),^[39] zeolites (SiO₂, Al₂O₃),^[40] molecular sieves (Figure 7)^[41] and alumina membranes (Fig-

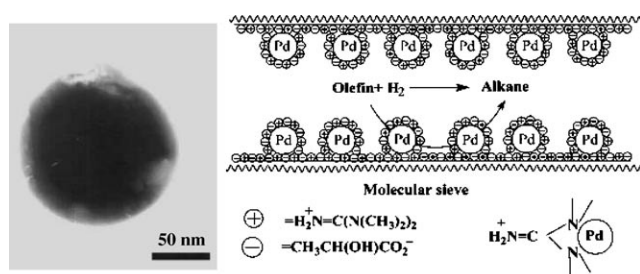


Figure 7. Transmission electron micrograph (left) of a molecular sieve with supported PdNPs (right). The catalyst, active in hydrogenation of olefins, contains 20 wt% ionic liquid as the stabilizer whose average layer thickness is 0.4 nm.^[41b]

ure 8).^[36a] Thus, despite the large variety of supports, the majority of them deal with a form of silica. The catalytic reactions examined with these supported NPs are hydro-

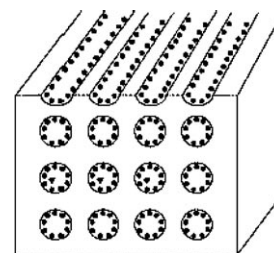


Figure 8. Schematic representation of a section of alumina membrane loaded with metal nanoparticles as would be used for the gas-phase catalysis of 1,3-butadiene hydrogenation (PdNPs) and CO oxidation (RuNPs).^[36a]

genation reactions, including selective ones, of unsaturated substrates, Heck and other C–C coupling reactions, and oxidation of CO and alcohols using molecular oxygen. The heterogenization of polymer- or dendrimer-stabilized NPs on a solid supports such as silica brings the classic advantages of heterogeneous catalysis, that is, stability to high temperatures, easy removal from the reaction medium, and the bottom-up approach of NP synthesis. A few outstanding recent examples are discussed below, and Table 1 gathers references for each NP-catalyzed reaction.

PtNPs and bimetallic dendrimer-stabilized Pd–AuNPs were adsorbed onto a high-surface silica support and thermally activated to remove the dendrimers (Figure 9). The Chandler group showed that these NPs were smaller than 3 nm and highly active for CO oxidation catalysis near room temperature. The hydrogenation of toluene was also efficiently carried out.^[34] The fabrication of uniform hollow spheres with nanometer to micrometer dimensions having tailored properties has recently been intensively studied using various procedures.^[42] Monodisperse palladium nanospheres of 300 nm catalyzed Suzuki coupling of iodothiophene with phenylboronic acid using 3 mol% Pd catalyst in ethanol under reflux. Under the same conditions 15 mol% Pd catalyst was used to couple bromobenzene (Figure 9).^[35b] Treating hydroxyapatite, [Ca₁₀(PO₄)₆(OH)₂], with [PdCl₂(CH₃CN)₂] gives a monomeric PdCl₂ species chemisorbed on the hydroxyapatite surface that, in the presence of alcohol, is readily transformed into supported PdNPs with narrow size distribution. These PdNPs catalyze the oxidation of 1-phenylethanol under atmospheric O₂ pressure in solvent-free conditions with very high turnover numbers of up to 236 000 and a remarkable turnover frequency of 9800 h⁻¹. The work up is easy and the catalyst is recyclable without requiring additives to complete the catalytic cycles.^[38]

Hydrotalcite anionic clays are layered double hydroxides of formula M²⁺_{1-x}M³⁺_x(OH)₂(Aⁿ⁻)_{x/n}·yH₂O (where Aⁿ⁻ is CO₃³⁻, Cl⁻, or NO₃⁻) in which the anion can easily be exchanged. These materials, after calcination at temperatures over 723 K, serve as supports for noble-metal catalysts, for example, C–C coupling^[39d] and selective semi-hydrogenation

Table 1: Overview of metal-nanoparticle-catalyzed reactions.

Reaction	Ref.	Reaction	Ref.
<i>Hydrogenations</i>			
Simple olefins and dienes	[2, 6b, 10d–i, 12, 14d,f,j,k,l, 16, 17a,b, 22b–d, 23, 26, 31l,o–q, 32, 33, 35a,i, 36a, 40a, 41, 43d, 44b,h, 46a–d, 58, 61]	Amination of aryl halides and sulfonates ($\text{ArX} + \text{RNHR}' \rightarrow \text{Ar-N(R)R}'$)	[44k–o, 74b, 77]
Alkynes	[14c, 37b, 39, 40b, 62, 63]	Hydrosilylation	[9h, 48]
CO ₂	[10, 82]	Coupling of silanes	[28a,b]
Arene rings	[12a, 29, 33k,m, 34, 37b, 65–70]	Hydroxycarbonylation of olefins	[75]
Arene rings of bibenzo-[18]crown-6	[64]	[3+2] Cycloaddition	[55]
Acrolein	[12b, 78]	McMurry coupling	[56, 57]
Methylacrylate	[16]	<i>Oxidation reactions</i>	
Allylic alcohols	[14d, 17b]	CO	[8a, 9d,e, 11j, 17, 34, 36a,b,e, 37c,d, 45, 50b, 80]
<i>N</i> -isopropylacrylamide	[17b]	Dihydrogen	[46f]
Ethylpyruvate	[30a, 63]	Aromatic amines	[33g, 46g]
Citral	[32c,d,e]	Alkyl amines	[9d]
Styrene	[18j]	1-Phenylethanol	[38]
<i>trans</i> -Stilbene	[32h,f]	CH ₃ OH elektrooxidation	[47]
Opening of epoxides	[14a]	Cyclooctane	[49]
Dehydrolinalole	[14b]	Cyclohexane	[46n]
Citronellal	[59b]	Ethene und propene epoxidation	[50]
9-Decen-1-ol	[35n]	Glucose	[51, 46m]
Functionalized olefins	[9f,g, 14e, 22b,d, 32h, 33k,m]	Diol, glycerol, ethylene glycole	[46c,e, 81]
Polar olefins	[22b]	Oxalate	[46m]
Nitroaromatics	[9a, 59c, 61]	<i>Aminations</i>	
Ketones, benzonitrile	[14h, 33l, 35d,i]	[24b, 43j]	
Cinnamaldehyd	[47, 59a]	<i>Carbonylations</i>	
Asymmetric hydrogenation	[29]	Aryl halides	[24b]
<i>Coupling reactions</i>		Methanol	[52]
Heck coupling ($\text{ArX} + \text{olefin} \rightarrow \text{arylolefin}$)	[7, 8b, 14f, 17f, 18i, 22, 24a, 31a–n, 32n, 33e–g,i,j, 35g,n, 40b, 43a–f, 44a–k, 53, 71–73]	<i>Miscellaneous reactions</i>	
Suzuki coupling ($\text{ArX} + \text{Ar}'\text{B}(\text{OH})_2 \rightarrow \text{Ar-Ar}'$)	[13a,b, 14i, 17i–k, 21–23, 24a, 25–27, 31m,n, 33e,h,i, 34b, 35b,o, 43c, 44c–e,l, 54, 72f, 74a, 76]	Allylic alkylation	[30f, 31, 35c, 57]
Sonogashira coupling ($\text{ArX} + \text{alkyne} \rightarrow \text{arylalkyne}$)	[28c, 43g,h,i]	Mannich reaction	[57]
Stille coupling ($\text{ArX} + \text{Bu}_3\text{SnR} \rightarrow \text{Ar-R}$)	[33h]	Pauson–Khand reaction	[11h, 35c]
Negishi coupling ($\text{ArCl} + \text{RZnX} \rightarrow \text{Ar-R}$)	[44m]	Hydroconversion of hydrocarbon	[40a]
Kumada coupling ($\text{ArCl} + \text{RMgX} \rightarrow \text{Ar-R}$)	[44j,k]	Combustion: alkanes, arenes, alcohols	[32e, 35j, 79]
Dehydrohalogenation of aryl-halides	[44i,n]	Methanol reforming	[36c, 39g]

of alkynes^[39e] have been obtained. Immobilization of a PdNP catalyst on a solid surface such as molecular sieves was achieved by using the ionic liquid 1,1,3,3-tetramethylguanidinium lactate. This system was used for solvent-free hydrogenation of alkenes and gave high activity and stability (for instance with a cyclohexene/palladium mol ratio of 12000:1, 100 % conversion was obtained in 10 h at 20 °C with a TOF of 20 min⁻¹).^[41b] The PdNPs whose size remains unchanged (1–2 nm) during the catalysis, are stabilized by guanidinium ions.^[33d] Ag–PdNPs prepared directly in ultrathin TiO₂ gel

films by a stepwise ion-exchange/reduction method showed an activity in methyl acrylate hydrogenation 267-times higher than commercial palladium black and 1.6-times higher than PdNPs that did not contain Ag. This outstanding activity was explained by the large fraction of the surface-exposed palladium atoms.^[57c] Polyelectrolyte multilayers serve as supports the PdNP catalysts for the selective hydrogenation of allylic alcohols, a reaction in which the isomerization is suppressed. To prepare this catalyst, polyacrylic acid and a polyethyleneimine palladium(II) complex were alternatively

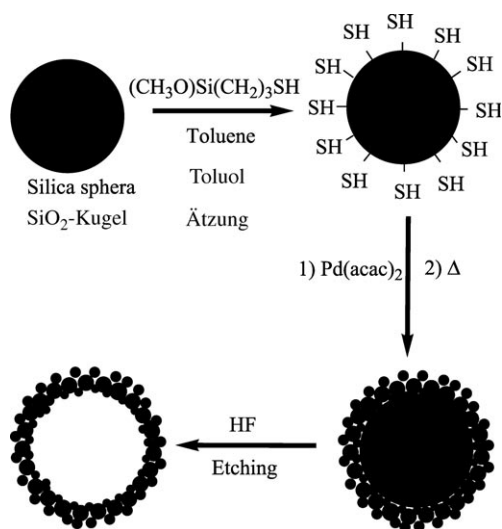


Figure 9. Principle of the formation of hollow PdNP spheres used for the catalysis of Suzuki reactions in refluxing ethanol with K₃PO₄ as a base. With 2-iodothiophene and phenylboronic acid (cat: 3% Pd spheres), at least seven cycles could be achieved with 95–97% yields, ref. [35b].

adsorbed on 150-nm diameter alumina particles, and subsequent reduction of Pd^{II} to PdNPs was carried out using NaBH₄.^[14d]

The mechanisms of oxide-supported PdNP catalysis are a long way from being understood. The oxide support however has a strong influence on the activity. For instance, in the Heck reaction, the activity is dominated by the support in the order: C (84%) > H-Mordenite (83%) > ZrO₂ (49%) > TiO₂ (45%) > MgO (37%) = ZnO (37%) > SiO₂ (7%). The good activity of zeolites in this reaction is seemingly due to a better stabilization of the active species in the cavities and to a better dispersion of PdNPs on the oxide support. There are many heterogeneous-catalysis studies that discuss the influence of parameters (solvent, catalyst, base, temperature, recycling activity, NP size). Indeed, Djakovitch and Köhler have proposed that, since the results are often similar for homogeneous and heterogeneous systems in terms of selectivity, the “heterogeneous mechanism” proceeds by leaching of molecular palladium species into the solution (a phenomenon favored in DMF). On the other hand, dehalogenation is more favored on a heterogeneous support than with a homogeneous catalyst. Thus, it has been proposed that supported PdNPs are responsible for dehalogenation.^[43]

The heterogeneous palladium-catalyzed Heck reaction has been extended to important α -arylated carbonyl derivatives, and the model arylation of diethylmalonate has been examined. The NaY-supported PdNP catalyst showed a limited activity, giving yields comparable to those obtained with the homogeneous (Pd(OAc)₂/4PPh₃) system, but the palladium concentration used is only 2% and the recyclability is good. The amination of halogenoarenes has also been investigated with MgO-supported PdNPs and ZrO₂-supported PdNPs, the amphoteric supports give the best yields, which would indicate that they favor the rate-limiting C–N

coupling in the reductive-elimination step. For this reaction, the zeolite supports give a better *para* selectivity presumably because of the “shape selectivity” properties of this material.^[43]

The Heck and Suzuki reactions have also been catalyzed by alumina-supported RuNPs.^[43c] Hydroxyapatite-supported RuNPs were recently found to be efficient and recyclable catalysts for *cis*-dihydroxylation and oxidative cleavage of alkenes.^[43d] Supported RuNPs in the pores of mesoporous Al-MCM-41 materials were prepared by H₂ reduction of adsorbed [Ru(NH₃)₆]²⁺. Their activity in benzene hydrogenation reactions was studied and found to be more efficient when 330 ppm H₂S was added to the H₂ than when H₂S was not present.^[43d]

Little is known concerning the catalytically active species of oxide-supported NPs, and it is possible that the supported NPs are only reservoirs of much smaller catalytically active palladium fragments.

5.2. Carbon Supports

Charcoal is a classic commercial support for catalysts, (for example Pd/C). Using the general synthetic method developed by Bönemann (the reduction of quaternary ammonium salts of metal cations in THF) the charcoal is impregnated simply by stirring in the NP suspension. These charcoal-supported metal NPs have been used for a variety of catalyzed reactions.^[7,29a,35a,41a,c] This procedure was also used by Reetz et al. to support their electrochemically prepared metal NPs including catalytically active bimetallic NPs.^[8,35a] Activated carbons that are suitable as support materials in catalytic processes need to be prepared and modified so that adequate surface area, porosity, and pore size distribution are obtained. Purification by acid treatment and elution processes are required to remove ash, extractable sp³ material, and contaminants. Treating and conditioning supports leads to optimal interactions between the precious metal and the support during impregnation and ensures dispersibility in the reaction media.

The detailed identification of the specific properties of the surface atomic layers of carbonaceous supports used for the preparation of Pd/C catalysts has been studied recently by means of inelastic incoherent neutron scattering. This technique allows the behavior of activated carbons and carbon blacks in the presence of adsorbed hydrogen to be studied and the vibrational states of protons on and inside carbon-supported PdNPs and PtNPs to be identified.^[44a] Well-known and typical applications of such materials are the hydrogenation reactions that are important for the synthesis of fine-chemicals intermediates, vitamins, and pharmaceuticals.^[2,44b] Such Pd/C catalysts were also reported for the Suzuki and other C–C forming reactions.^[44c–e]

It was shown that the catalysis proceeds with palladium dissolution/precipitation, the palladium concentration in solution being highest at the beginning of the reaction and minimal (< 1 ppm) at the end of the reaction. The mechanism is quasi-homogeneous, and small palladium species in solution act as the catalytically active species.^[44f,g] The palladium

is leached and, at the end of the reaction redeposited, which provides an excellent recovery of the precious metal from the reaction mixture.^[44f,g] The precipitation of the catalyst at the end of the reaction significantly changes its state and decreases its activity, however, making its reuse unattractive.^[44f]

Köhler et al. also showed that optimization of the Pd/C catalyst (temperature, solvent, base, and palladium loading) for the Heck reaction of unactivated bromobenzene at 140 °C, allows turnover frequencies (TOFs) of up to 9000 mole of product per mole of catalyst per hour (the highest ever reported) to be reached and palladium concentration down to 0.005 mol % to be developed. The efficiency of this catalyst is far higher than, for instance, palladium on mesoporous silica and palladium on zeolites, and TOFs are higher than homogeneous palladium catalysts. The turnover numbers (TONs), however, are surpassed by those of the best homogeneous catalysts.^[44f] As indicated above, the efficiency of the Pd/C catalyst strongly depends on the palladium dispersion, oxidation state in the fresh catalyst (in situ reduction of Pd^{II} to active Pd⁰ under the Heck reaction conditions leads to the best dispersion and activity), impregnation method, and pre-treatment. Interestingly, exclusion of air and moisture is not necessary, however. The fact that no dehalogenation of bromobenzene to benzene is found confirms the homogeneous mechanism, whereas surface heterogeneous catalysis might be responsible for dehalogenation under different conditions.

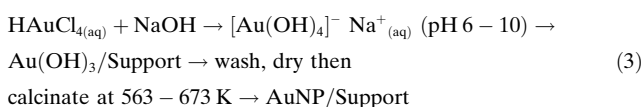
Heterogeneous Ni/C catalysis^[44h-o] is also mainly known for the hydrogenation of unsaturated compounds.^[44h] Recent reports, however, concern hydrodehalogenation of aryl halides (including aryl chlorides),^[44i,n] Kumada,^[44j,k] Suzuki,^[44l] and Negishi-type C–C coupling^[44m] and aromatic amination.^[44k-o] Whereas the mechanism for heterogeneous hydrogenation follows true surface chemistry with dihydrogen chemisorption onto the metal surface,^[44p] C–C and C–N coupling reactions involve nickel bleed from the carbon support, a one-time event at the very beginning of the reactions. There is an equilibrium for between homogeneous nickel species located inside and outside the carbon pores which strongly favors the former. Thus, unlike in the Pd/C case, only traces of metal are detectable in solution. The nickel is completely recovered on charcoal, making this heterogeneous catalyst interesting for applications. These reactions appear to be due to a combination of heterogeneous and homogeneous catalysis.^[44k,n]

Recently, new supports such as high-area carbon have been used to prepare bimetallic Pt–RuNPs that catalyze methanol electrooxidation with enhanced activities compared to commercial catalysts.^[46i-l] Pd-, Rh-, and RuNPs, deposited onto functionalized carbon nanotubes by hydrogen reduction of metal- β -diketone precursors are effective catalysts for hydrogenation of olefins, such as *trans*-stilbene in $s\text{CO}_2$.^[32g] Comparison of the properties of carbon nanotube and activated carbon supports were carried out for Heck and Suzuki reactions, aerobic alcohol oxidation, and selective hydrogenation.^[44q]

6. The New Gold Rush

In the AuNP-catalyzed CO oxidation to CO₂ by O₂ that can occur down to 200 K, the oxide support (Fe₂O₃, TiO₂ or Co₃O₄) is indispensable.^[9c,d] The mechanism is not clear, however.^[45a] A new “gold rush”^[9d,e,45] is now following Haruta’s crucial work on catalysis with AuNPs.^[9c,d] This finding of low-temperature catalysis of CO oxidation is of great interest, because the Pt/Pd catalysts that are currently used in cars for CO oxidation work only at temperatures above 200 °C. Thus, CO pollution essentially occurs during the first five minutes after starting the engine. The low-temperature, supported-AuNP-catalyzed CO oxidation clearly could solve this problem.

CO can be selectively oxidized by O₂ in the presence of H₂ which allows H₂ to be purified from residual CO. There are many other challenges in catalytic oxidation chemistry that can be addressed using this type of catalyst (see below). Of the various ways to prepare supported AuNP catalysts, it is considered that Haruta’s deposition–precipitation procedure is the most suitable [Eq. (3)].^[9d]



The optimum size of the AuNPs is 3 nm, stable hemispherical NPs, are formed, their size being controlled by the calcination temperature (optimum 570 K). The best support is TiO₂, for a good dispersion of the AuNPs the addition of Mg citrate is necessary during or after coprecipitation).

It has been shown that oxidation of CO by O₂ to CO₂ can also be catalyzed in the gas phase by the cluster Au₆[−] (Figure 10),^[45c] and calculations with Au₁₀ predict CO oxidation by O₂ below room temperature.^[45d] Although the mechanism was thus depicted with AuNPs alone^[45c,d] (Figure 10), the activation by the oxide support is also

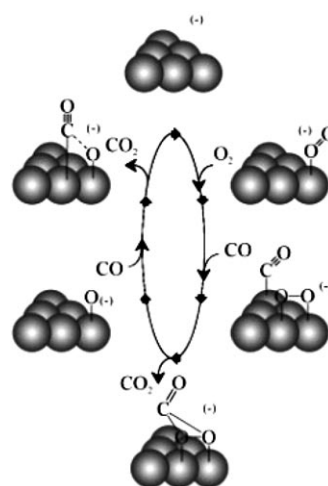


Figure 10. Proposed schematic mechanism of the Au₆[−] catalyzed formation of CO₂ from CO and O₂ in the gas phase (Reprinted with permission from ref. [44c].)

needed and must be involved in the mechanism. It is probable that the oxide favors the polarization of the adsorbed CO molecule to provoke electrophilic attack on the CO carbon atom by AuNP-support-activated O₂ (in the form of superoxide or a related nucleophilic oxygen species).^[9d,e,45b] It is also suggested that CO adsorbs on the edge and step sites of AuNP surfaces and O₂ adsorbs on support surfaces.^[50b]

Applications of supported AuNPs are expected both in the catalytic removal of CO produced at ambient temperature by engines and in the removal of CO traces from dihydrogen streams feeding the fuel cells. There has been a tremendous increase recently in the number of reports focusing on this area of supported AuNP-catalyzed CO oxidation, TiO₂ becoming the dominant support.^[45] Besides CO oxidation, other supported-AuNP-catalyzed reactions have been disclosed, confirming that supported AuNPs are now a very popular means to catalytically activate dihydrogen and dioxygen. The following applications have been reported:

- Hydrogenation of 1,4-butadiene to butenes,^[46a] acrylaldehyde to allylic alcohol,^[46b] citral to geraniol and nerol,^[46c] and benzalacetone to phenyl-3-butene-2-ol.^[46d]
- Oxidation (using O₂ or air) of alcohols to aldehydes,^[46c] *o*-hydroxybenzyl alcohol to salicylic aldehyde,^[46d] ethane-1,2-diol to glycolate,^[46c] other diols to hydroxymonocarboxylates,^[46c] β-amino alcohols to β-amino-acids,^[46c] aliphatic aldehydes to carboxylic acids,^[46c] D-glucose to gluconic acid^[46e] or oxalate,^[46m] dihydrogen to hydrogen peroxide,^[45f] aromatic amines (with CO) to carbamate,^[46g] propene to propene oxide,^[45h] and cyclohexane to cyclohexanol and cyclohexanone.^[46n-o] Alcohols, in particular methanol, are also oxidized electrochemically, with supported AuNPs being more active electrocatalysts than AuNPs alone.^[47]

Other applications of supported AuNP-catalyzed reactions are numerous. They include:

- Oxidative decomposition by Fe₂O₃-supported AuNPs of bad-smelling alkylamines responsible for unpleasant atmosphere in toilets.^[9d]
- Oxidative decomposition of dioxin coming from incinerator outlet gases by La₂O₃-supported AuNPs integrated with Pd/SnO₂ and Ir/La₂O₃.^[9d]
- Direct epoxidation of propylene to propylene oxide by TiO₂(MCM48)-supported AuNPs.^[9d]
- Sensors using Co₂O₃-supported AuNPs that are able to simultaneously detect H₂ and CO at low concentration levels.^[9e]
- CO safety masks for efficient removal of CO from contaminated atmospheres.^[9e,45f]
- Various liquid-phase synthetic processes.

7. Summary of Mechanistic Information

Hydrogenation of unsaturated substrates under ambient conditions can be catalyzed by a large variety of unsupported

or supported metal NPs of 1 to 5 nm size and, in the mechanistically studied cases, proceeds by the classic heterogeneous surface mechanism involving dihydrogen chemisorption. The use of core-shell bimetallic NPs, where by the metal core activates the metal surface of the NP, improves the catalytic efficiency compared to the monometallic NPs. For soluble metal NPs active at room temperature, hydrogenation presumably proceeds on the edge of polyhedral NPs without leaching.

The finding that dehalogenation of halogenoarenes occurs in the course of heterogeneously catalyzed C–C bond-formation reactions is explained by a heterogeneous mechanism.^[43] It has been proposed that defects on the PdNP surface are involved in the mechanism of C–C bond formation in the Heck reaction, that is, the activity should be related to the number of low-coordinate surface atoms.^[83] It has also been suggested that flat π-adsorption of the aromatic ring of the aryl halide over a “large” PdNP is responsible of activation of the C–X bond prior to formation of a σ-aryl-palladium complex at the PdNP surface.^[84] However, the homogeneous mechanism according which the catalytic activity is due to palladium species leaching from the heterogeneous catalyst (Pd/C or Pd/MO_x) into the solution is presently preferred. This “leaching mechanism”,^[43,85,86] first proposed by Julia et al. in 1973,^[85] is now firmly established especially by the recent work by Djakovitch and Köhler using astute experiments in which the selectivities obtained in homogeneous and heterogeneous catalysis are compared.^[43e] Charcoal-supported catalysts are superior to oxide-supported catalyst in terms of efficiency and selectivity. PdNPs on NaY zeolites are also very efficient catalysts, and the catalytically active Pd⁰ species could be retained in the zeolite pores or re-adsorbed at the surface by dissolution–readsorption.^[43e,f] The thermal treatment has an important influence on the mechanism, as Pd^{II} species surrounded by oxygen atoms in the zeolite pores could give leaching whereas Pd⁰NP entrapped the zeolite pores would still react by a heterogeneous mechanism.^[87a] The exact nature of these exceedingly reactive species involved in the homogeneous mechanism is not known: they could be mono- or bimetallic metal species^[87b] or very small metal clusters containing only a few atoms. They could be neutral or be coordinated to an anionic ligand (for example, halide, acetate) making them anionic which could facilitate the oxidative addition of the aryl–halogen bond.^[88]

The finding that unsupported palladium salts are active even under “homeopathic” (extremely low) concentration in the “absence” of ligand (except halide or acetate) was taken together with the facts that PdNPs were confirmed and that dilution improved the catalysis led Reetz to propose an equilibrium between PdNPs and catalytically active palladium fragments.^[31j,n] Thus, in the Heck reaction, there is a good parallel between homogeneous catalysis and catalysis by supported PdNPs. In the homogeneous case, the PdNPs are the reservoir of active palladium species, and in the supported Pd/C catalysis, the charcoal or zeolite is the reservoir of palladium species that are also catalytically active in solution. These active species could be of similar nature in both supported and unsupported cases.

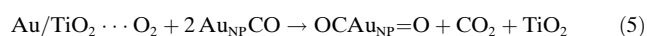
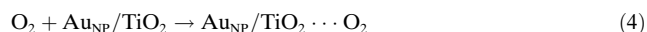
Such a mixture homogeneous and heterogeneous catalysis was also found for Ni/C catalysis of a variety of C–C and C–N coupling reactions (Kumada, Suzuki, Negishi, Heck, amination of bromoarenes). The leaching of nickel species was demonstrated in all these cases. However, the amount of leached metal is much less important than in the palladium case; with nickel the amount of leaching remained essentially constant and extremely low throughout the reactions. Besides supported NP metal catalysts, some unsupported, but ligand-coordinated PdNPs are active and recyclable catalysts for the Suzuki C–C coupling reaction at room temperature.^[27] It is possible that, under such mild conditions, the PdNPs do not lose palladium atoms or clusters of atoms in the solution, and that catalysis occurs at the edge of the polyhedral PdNP itself, but this remains to be ascertained.

It is clear that care should be exercised in classifying the NP-catalyzed reactions as homogeneous or heterogeneous as the frontier is fuzzy, as exemplified by the above homogeneous mechanism of reactions on heterogeneous supports.

Techniques that allow investigation of the leaching of metal species from the supported metal to the solution are crucial to mechanistic investigations and include transmission electron microscopy (TEM), energy dispersion X-ray analysis (EDX), and X-ray diffraction. Data are recorded from samples before and after catalytic runs for comparison. Sometimes, experiments carried out with and without PPh₃ or a polymer phosphine are compared to investigate the importance of such ligands on the activity of the leached metal species in solution. The metal content in solution can also be determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) after filtration of the hot or cooled reaction mixture. Comparison of the selectivities obtained with homogeneous and heterogeneous catalysts is also a powerful means to investigate whether heterogeneous catalysis proceeds by an active leached species.^[43e]

Concerning the important AuNP catalysis of CO oxidation by O₂, recent studies by Haruta's group indicate that the TOF increases with decreasing AuNP diameter. The enhancing effect of moisture on the metal oxide support was demonstrated. Kinetic studies showed that the rate of CO oxidation is independent of the CO concentration and only slightly dependent on the O₂ concentration in the low concentration range down to 0.1 vol%. This result suggests that both CO and O₂ are adsorbed on the catalyst surface to near saturation and that the rate-determining step is the reaction between the two adsorbed species. Isotope effects also are a useful technique contributing to mechanistic investigations. Some logical mechanistic trends are apparent and have been proposed, in particular by Haruta, although the precise mechanism is unknown and still the subject of scrutiny. Adsorption of CO and O₂ must occur at the NP periphery on edges and corners. The Au-coordinated CO must be polarized (C^{δ+}–O^{δ-}) upon coordination, and the dioxygen molecule must also be polarized or reduced to the superoxide anion by AuNPs. Then O₂⁻ could attack the positively polarized CO carbon atom. The role of the oxide support might be to facilitate the polarization of either molecule or both, this role however is more difficult to evaluate. The support may also have a crucial role in the

cleavage of the superoxide species or negatively polarized oxygen atom of the O₂ molecule before, during, or after CO binding.^[45] Haruta recently depicted his mechanistic proposal as follows [Eq (4)–Eq (6)].^[11j]



Clarification should be provided by theoretical work involving not only AuNPs but all the four components of the reaction including the TiO₂ support. Intriguingly, the Corma group reported that Au³⁺ on CeO₂ catalyzed the homocoupling of phenylboronic acid, and the catalytic cycle was proposed to involve the interconversion of Au³⁺ and Au⁺.^[87c] Spectroscopic studies, by the same research group, of Au supported on nanocrystalline CeO₂ showed that CO was bonded to Au³⁺, Au⁺, and Au⁰ species, whereas the active form of O₂ was bonded to CeO₂ as superoxide η¹-O₂⁻, confirming the nucleophilic attack on the electron-deficient carbon atom of CO by superoxide on the way to CO₂.^[87d]

8. Prospects for Organic Synthesis

The discovery of the catalytic formation of C–C and C–N bonds by palladium catalysts has been a considerable advance for organic chemistry. It became possible to easily functionalize olefins, alkynes, and aromatics. Yet, the problems of catalyst recovery and pollution by phosphines were unsolved. These aspects are crucial for the pharmaceutical industry, because the presence of metal and phosphine contaminants in drugs is unacceptable. These problems are largely solved by the use of Supported NP catalysts which allows catalyst removal from the reaction mixture by simple filtration. The carbon and NaY zeolite supports (the best ones) are reservoirs of metal species that retain these metal species subsequent to reaction in solution. The amount of metal left in solution is in the ppm range. Moreover, such types of catalyst are phosphine free. The firm DSM employ this method for the synthesis on the kg-scale of pharmaceutical intermediates, and it is likely that this type of procedure will find use throughout the pharmaceutical and other industries.

The Heck reaction is a key reaction in the production of fine chemicals on multiton scale per year^[89] for which the use of NP catalysts could be possible. It is used for the production of the herbicide prosulfuron,^[90] the anti-inflammatory naproxen,^[91] or the anti-asthma singulair.^[92] On the other hand, in terms of "Green Chemistry", it is likely that procedures involving chemicals such as ionic liquids, micelles, surfactants, and other additives in homogeneous solution will be of interest.

Given the extraordinary recent advances in AuNP-catalyzed reactions, it is clear that many applications in oxidation catalysis will very soon penetrate the every-day world of organic chemists. In addition there is considerable interest from materials scientists for the reduction of car

pollution and in H₂ purification through the removal of residual CO.

9. Conclusion

The design and use of metal NP catalysis is now well advanced thanks to the efforts of pioneers and advent of modern characterization techniques. A large variety of NP preparation modes, a variety of materials that can serve as supports or grafting cores, and several media are available. Monodisperse, small (1–10 nm) supported metal NPs are available for many important reactions. Bi- and trimetallic NP catalysts are often more efficient than those containing only one type of metal. Compared surface studies on palladium single crystals and PdNP have even shown that alkene hydrogenation is only catalyzed by PdNPs.^[32] These advances have considerably improved the selectivity of NP-catalyzed reactions, especially the heterogeneously catalyzed hydrogenation of unsaturated substrates. High enantioselectivity has been obtained, although it has not yet been demonstrated that asymmetric induction occurs at the metal NP surface and not on more reactive leached monometallic complex fragments. For example, in the Pd/C and Ni/C catalyzed C–C and C–N bond forming reactions, the mechanism involves such a leaching pathway with recovery of the metal on the support at the end of the reaction. More mechanistic studies are called for to understand the nature of the very active metal species in solution. The activation of aryl chlorides for C–C coupling reactions still remains a key challenge because organometallic catalysts are presently more efficient than metal NP catalysts. A major recent finding was the removal of these NP catalysts by filtration, although recycling and efficient re-use many times of supported NP catalysts remains a challenge.

Altogether, the field of metal NP catalysis is a fascinating one, as exemplified by the new gold rush and its very attractive perspectives in oxidation chemistry and by the ligand-free palladium and nickel catalysts that are employed in “homeopathic” amounts. The metal NP field is presently expanding dramatically, and it is anticipated that these key challenges will be met in the near future, and that this area will find many more applications in tomorrow’s laboratory and industry.

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