Review

Applied
Organometallic
Chemistry

Received: 7 January 2008 Accepted: 14 January 2008

(www.interscience.com) DOI 10.1002/aoc.1382

Transition-metal nanoparticles: synthesis, stability and the leaching issue

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This perspective examines the state-of-the-art of catalysis by metal nanoparticles. We outline various methods for preparing metal nanoparticle suspensions, and highlight the role of the stabilizers and the stabilizing principles. Subsequently, we examine some catalytic applications of homometallic and bimetallic nanoparticle suspensions in a variety of reactions. The cases are divided according to the stabilizing agent: polymers, dendrimers, ionic liquids, surfactants, micelles and micoremulsions, ligands and solid supports. We explain the importance of atom/ion leaching (all too frequent in nanoparticle catalysis, especially for the catalytically active group VIII metals) and consider ways of minimizing it. The future perspectives of nanoparticles as catalysts are discussed. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: nanocolloids; catalysis; polymers; dendrimers; ionic liquids; micelles; microemulsions; ligands; supported catalysts

Introduction

The twenty-first century is in many ways the century of nanotechnology. Promises and possibilities are wide-ranging: nanometric catalysts open new routes to a variety of products,[1,2] nanomagnets will store information for superfast computers,[3] nanowires will string together nanoelectronic circuits[4,5] and nanomachines will transform modern medicine.[6] For all these applications, understanding and controlling the synthesis of metal nanoparticles is essential.

In the nanoscale regime, somewhere between the bulk solid and molecular state, metal particles show unique properties. Because of their small size, a high percentage of the atoms are surface atoms, leading to increased catalytic activity.[7] In heterogeneous catalysis, metal nanoparticles have been used for over 50 years.[8] One of the first processes to use such catalysts is catalytic reforming for the production of reformulated gasolines.[9] Industrial catalysts containing nanoparticles of 1 nm-Pt on chlorinated alumina were introduced in the 1960s[10] and Pt–Re or Pt–Su bimetallic catalysts (1 nm particles) in the 1970s.[11] In hydrogenation, hydrocracking and aromatization processes, zeolites exchanged with noble[12,13] and non-noble metals[14] are currently used. More recently metal catalysts were successfully employed in automotive catalytic converters.[15] Thus, the synthesis and application of metal nanoparticles in gas/solid systems is well established, and here we will focus on the application of nanoparticle suspensions, mainly in liquid phase systems.

As early as 1986, Lewis *et al*. envisaged the participation of Pt nanoparticles in catalytic hydrosylilation reactions.[16] Since then, noble–metal nanoparticle catalysts have appeared in numerous reports and reactions, from hydrogen peroxide decomposition[17] all the way to Heck cross-coupling.[18,19] Figure 1 shows a bar graph of the number of publications in peer-reviewed journals for nanoparticle (NP) catalysts for the last two decades. Several recent reviews cover the catalytic applications of NPs.[20–24] In this perspective, we will focus on the lastest developments, with a special emphasis on NP stabilizing and leaching issues.

Note that different sources refer to different things as 'nanoparticles', 'nanoclusters' and 'nanocolloids'.[25,26] To avoid semantic problems, we will use throughout this review the term 'nanoparticles' to denote any type of metallic species with a size between 1 and 25 nm.

Synthesis of Metal Nanoparticles

The various methods for synthesizing metal NPs were extensively reviewed by Bönnemann,[27] Schmid,[28] Aiken and Finke,[22] Roucoux,[21] Wilcoxon[29], Philippot and Chaudret[30] and Cushing.[31] In general, there are four main categories.

Reduction of transition metal salt precursors

Discovered 150 years ago by Michael Faraday, the 'wet chemical' reduction has become the most common method for making NPs.[32] The first reproducible synthesis was done by Turkevich and co-workers, who prepared 20 nm Au particles by citrate reduction of $[AuCl_4]^-$. [33,34] They also proposed a mechanism for the stepwise formation of NPs based on nucleation, growth and agglomeration.[35]

$$xM^{n+} + nxe^- + \text{stabilizer} \longrightarrow M^0{}_{n\ (\text{cluster})} \qquad (1)$$

In this approach [equation (1)] the reducing agent (e.g. hydrogen, alcohol, hydrazine or borohydride) is mixed with the metal precursor salt in the presence of stabilizing agents (ligands, polymers or surfactants). The latter prevent the undesired agglomeration and formation of metal powders (Fig. 2). The actual size of the NPs depends on many factors, including the type of reducing agent, metal precursor, solvent, concentration, temperature and reaction time.

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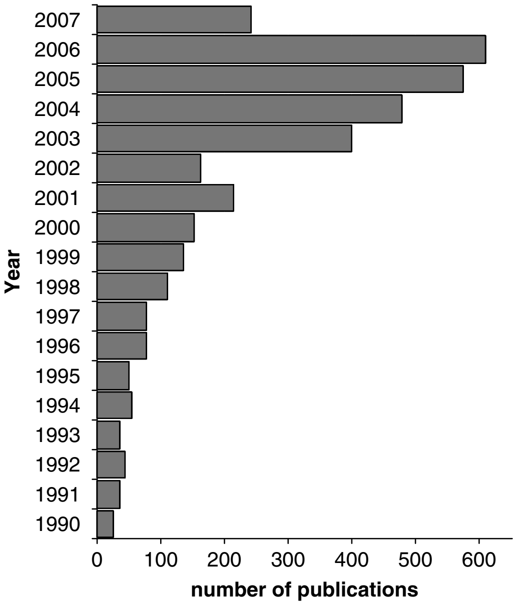

Figure 1. Bar graph showing the number of peer-reviewed journal papers containing the word 'catalysis' and one of the terms 'metal nanoparticles', 'metal colloids' or 'metal nanoclusters' in the title, keywords or abstract.

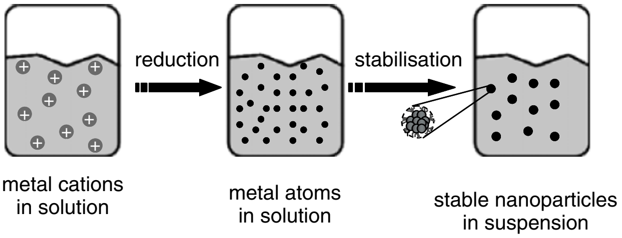

Figure 2. Formation of NPs via reduction of metal salt precursors.

Electrochemical synthesis

This method was developed by Reetz in the 1990s.[18,36] The overall process includes five steps (see Fig. 3):

1. Oxidative dissolution of the sacrificial metal bulk anode.
2. Migration of metal ions to the cathode.
3. Reductive formation of zerovalent metal atoms at the cathode.
4. Nucleation and growth of metal particles.
5. Arresting the growth process and stabilizing the NPs with protecting agents, e.g. tetraalkylammonium ions.

The electrochemical pathway avoids contamination with by-products resulting from chemical reducing agents, and the products are easily isolated from the precipitate. Further, it allows size-selective particle formation by tuning the current density: high current densities lead to small NPs, and vice versa. The particle size can also be controlled by adjusting the distance between the electrodes, the reaction time and temperature, or the solvent polarity.

This method was successfully applied in the preparation of a number of monometallic NP organosols and hydrosols, including Pd, Ni, Co, Fe, Ti, Ag and Au. Bimetallic alloys (e.g. Pd–Ni, Fe–Co and Fe–Ni) are accessible if two sacrificial metal anodes are used simultaneously.[37] Recently, we developed a reactor for synthesizing high surface area core/shell NPs, by combining electrochemical and 'wet chemical' methods (Fig. 4).[38]

$$M^0\ \textit{anode} \rightarrow M^{n+} + ne^-$$

$$M^{n+} + ne^- + \text{stabiliser} \rightarrow M^0\ \textit{(nanoparticle)}$$

$$M^0\ \textit{anode} + \text{stabiliser} \rightarrow M^0\ \textit{(nanoparticle)}$$

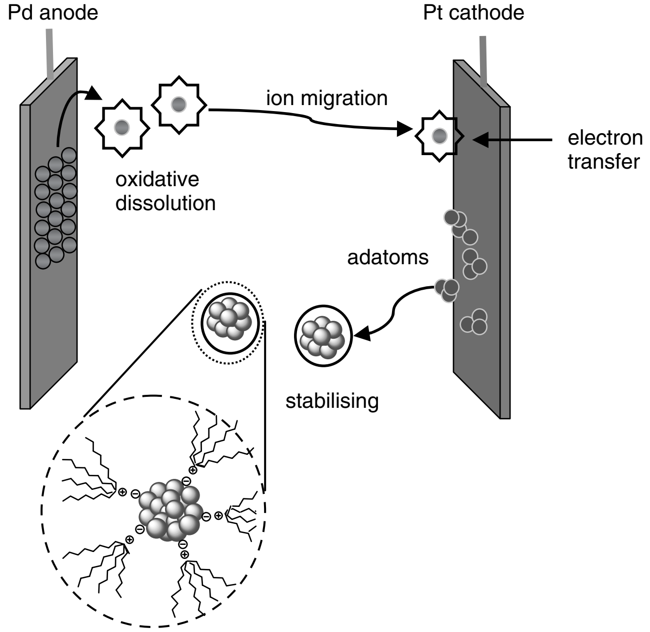

Figure 3. Electrochemical formation of $NR_4{}^+Cl^-$-stabilized Pd nanoparticles.

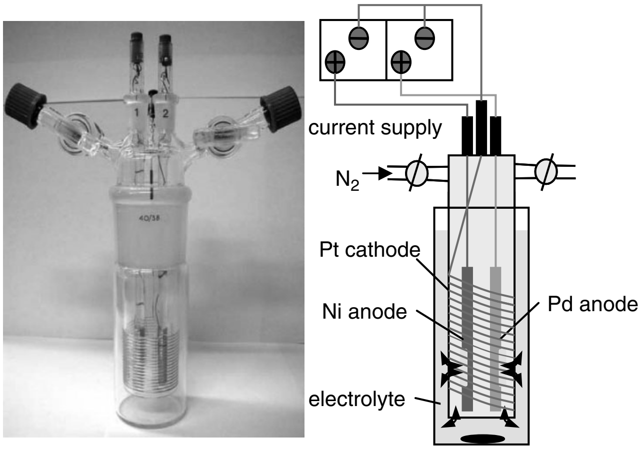

Figure 4. Photo and schematic of the two-electrode cell used for synthesizing core/shell NPs.

Reduction of organic ligands in organometallic precursors

Starting from low-valency metal complexes, the ligands are reduced typically with H_2, equation (2), or carbon monoxide. The reduced ligands leave the M^0 centre, allowing the clustering of metal atoms.[39]

$$nM(L)_x + xH_2 + \text{stabilizer} \longrightarrow M^0{}_{n\ \text{(cluster)}} + xLH_2 \qquad (2)$$

Metal vapour chemistry

The atomic vapour of a metal is condensed into a cold liquid, containing a stabilizer. Upon warming, the dissolved metal atoms form NPs. When the liquid itself acts as a stabilizer, the metal vapour can condense with the solvent vapour, giving a solid matrix.[40]

Other less common methods include redox surface techniques,[41,42] thermal[43] and photochemical[44] decomposition of metal complex precursors, sonochemical synthesis[45] and laser ablation.[46]

Stabilization of Metal Nanoparticles

Since 'naked' NPs are kinetically unstable in solution, all preparation methods must use stabilizing agents, which adsorb at the particle surface. There are three types of NP stabilization: in *electrostatic stabilization*, anions and cations from the starting materials remain in solution, and associate with the NPs. The particles are surrounded by an electrical double layer (Fig. 5, top). This results in a Coulombic repulsion that prevents agglomeration. In *steric stabilization,* aggregation is prevented through the adsorption of large molecules (e.g. polymers or surfactants) as shown in Fig. 5, bottom. The third option, combining both steric and electrostatic effects, is known as *electrosteric stabilization*.

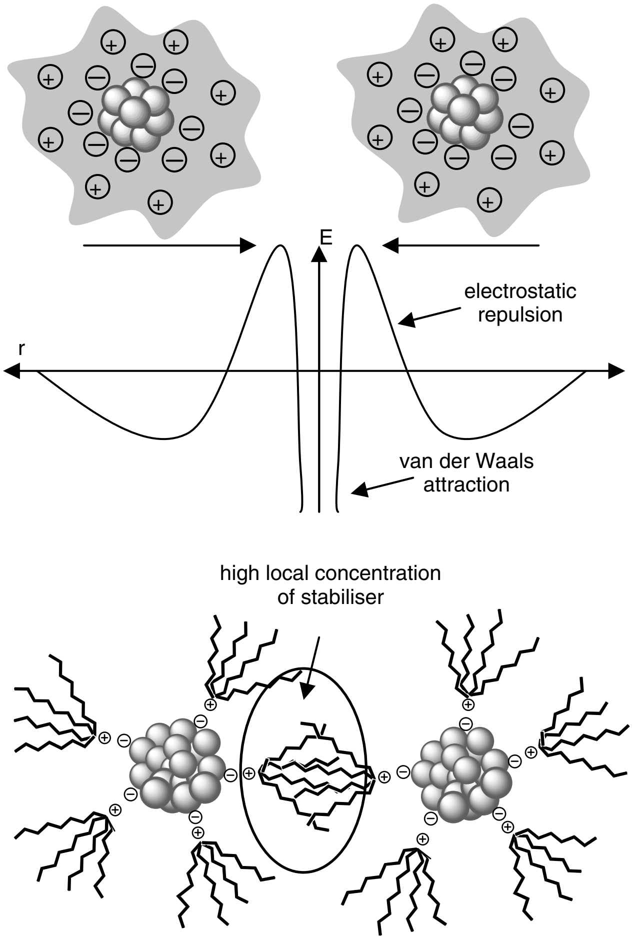

Figure 5. Electrostatic stabilization (top) and steric stabilization of metal nanoparticles (bottom).

Alternatively, one can anchor the NPs on a solid support.[25,26] This approach, which is popular as a method for catalyst preparation and heterogenization, will be discussed in detail below.

Atom/Ion Leaching – a Key Issue

Although metal NPs are frequently reported as 'ligand-free' catalysts, the fact that a system contains NPs does not necessarily mean that they are the true catalysts. In C–C coupling, for example, leaching of Pd atoms and/or ions is a key issue. NPs are definitely involved in the catalytic cycle – many of the so-called Pd-complex-catalysed coupling reactions, and especially those done above 120 °C, were later shown to be catalysed by either Pd atoms or ions. De Vries recently proposed a unifying mechanism for all high-temperature Heck reactions, showing that, regardless of the catalyst precursor type, Pd is reduced at 120 °C to Pd^0 and forms NPs.[47] There has been much scientific argument regarding the actual catalytic species. Bradley and co-workers[48] and El-Sayed[49] reported that low coordination sites on the clusters catalyse the reaction. Conversely, Schmidt,[50] Bhanage,[51] de Vries[47,52,53] and Reetz,[54] suggested a homogeneous mechanism in which the NPs act as 'reservoirs' of active Pd atoms or ions. In 2006, we proved, using a special membrane reactor, that Pd atoms and ions do leach from Pd NPs in Heck and Suzuki coupling reactions (Fig. 6).[55,56] This means that every report on NP catalysis must be examined carefully (see also the recent comprehensive review by Jones and co-workers[57]). For this reason, we exclude from this perspective several recent papers reporting NP-catalysed Heck, Suzuki and Sonogashira reactions, in which no leaching

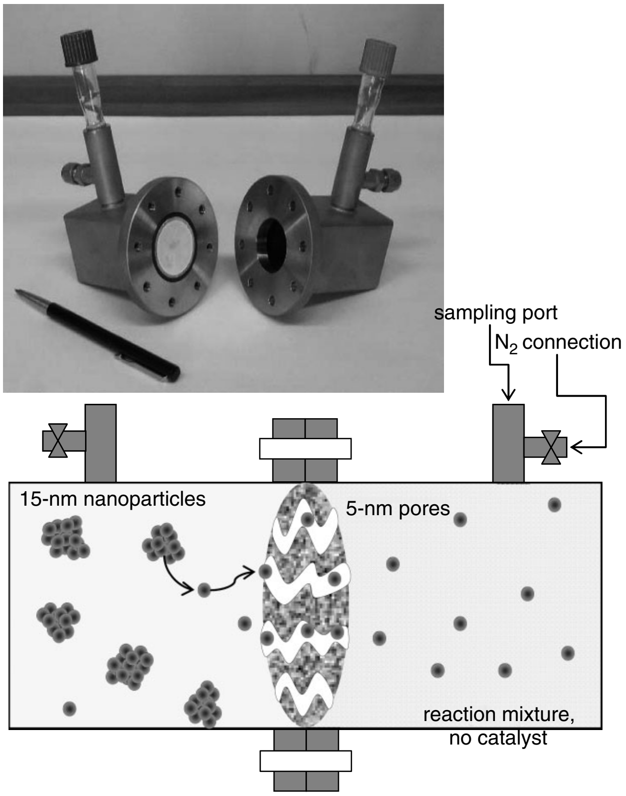

Figure 6. Photograph and schematic of the two-compartment membrane reactor used in the nanoparticle-exclusion experiments.

studies were done. Conversely, several papers show, mainly for hydrogenation reactions, that soluble metal precursors often form metal nanoparticles as the actual catalysts.[58,59] As we shall see, using solid supports or ionic liquids are two practical options for minimizing NP leaching.

Polymer-Stabilized NPs

Polymers are widely used in the NP synthesis, generally as steric stabilizers. They stabilize NPs through the steric bulk of their framework, but also by binding weakly to the particles surface through heteroatoms that act as ligands.[60] The stabilization efficiency of a polymer is given by its *protective value*.[61] The protective values of poly(*N*-vinyl-2-pyrrolidone) (PVP), poly(vinyl alcohol), poly(acrylamide), poly(acrylic acid) and poly(ethyleneimine) are 50.0, 5.0, 1.3, 0.07 and 0.04, respectively.

PVP is commonly used because it is non-toxic and soluble in many polar solvents.[62] As Fig. 7 shows, part of the PVP adsorbs on the NP surface, while the other part dissolves freely in the suspension, creating a second protective shell. Both concentrations are important for controlling the NP size.[61] Two groups reported the synthesis of NPs in aqueous solutions using PVP as stabilizing *and* reducing agent.[63,64] This method gave stable Ag and Au hydrosols, and simple variations of the PVP–metal ratio yielded structures with very different shapes and sizes.

The effect of size and stability in the catalytic activity of PVP-stabilized NP catalysts was examined by El-Sayed *et al.*[49,65] for Suzuki reactions in water. Smaller particles showed higher activity, suggesting that the low-coordination-number vertex and edge atoms are the active catalytic sites. Tsukuda and co-workers supported this theory, reporting the NP size effect in catalysis in the aerobic oxidation of benzylic alcohols catalysed by monodisperse Au NPs stabilized by PVP.[66] The Au particles are weakly stabilized through multiple coordination of the <N–C=O groups.

The disadvantage of using PVP is the separation of the catalytic particles from the product and unused reactants at the end of the reaction.[67] To solve this problem, Mu *et al.*[68] used PVP-stabilized Pt-, Pd- and Rh NPs immobilized in an ionic liquid, 1-*n*-butyl-3-methylimidazolium hexafluorophosphate. These NPs were synthesized by reducing the corresponding metal halide in refluxing ethanol, giving a narrow size distribution that depended on the metal–PVP ratio. They showed good catalytic activity and stability in the hydrogenation of olefins under mild conditions. The hydrogenation products were easily isolated from the ionic liquid phase by decantation. The catalyst was recycled several times without loss of activity. Note that immobilizing NPs on a solid support decreases their activity, due to geometrical restriction of the particles in the solid. Using ionic liquids may avoid this problem.[21]

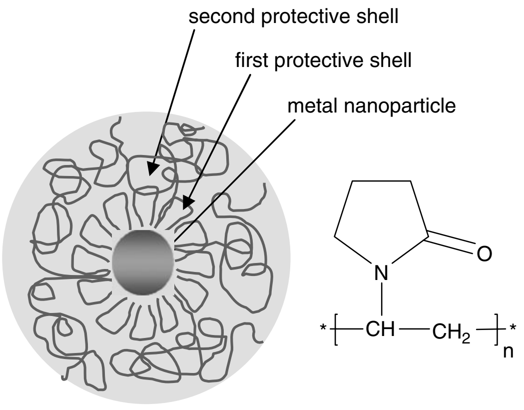

Figure 7. Conformation model of PVP-stabilization of metal nanoparticles.

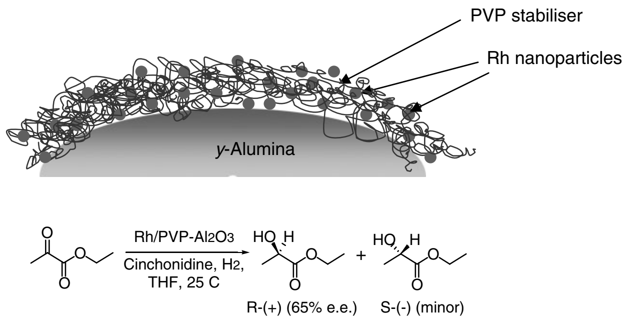

Figure 8. Enantioselective hydrogenation of ethyl pyruvate by Rh/PVP-alumina nanoparticles (1.8 nm).[71]

Several groups combined PVP-stabilized NPs and chiral modifiers as enantioselective catalysts. The PVP–Pt–cinchonidine combination gave >95% *ee* in the hydrogenation of α-ketoesters.[69] Other transition metals, such as Ru, Rh, Pd and Ir, yielded 20–30% *ee*.[70] This was improved to 65% *ee* by supporting Rh NPs stabilized by PVP on alumina *micro*-particles, using cinchonidine as the chiral modifier (Fig. 8).[71]

Favier *et al.*[72] reported Pd, Pt and Rh NPs stabilized by main chain chiral polymers. The commercial polymer Gantrez (GAF) was chirally fuctionalized using borneol, aminobutanol or α-methylbenzylamine. Polyacrylates were also prepared containing amino and ammonium groups, to obtain water-soluble polymers. The NPs were synthesized by decomposition of organometallic compounds or metallic salts, under hydrogen atmosphere. Preliminary studies show their potential in catalytic asymmetric hydrogenation in water.

Schubert and co-workers prepared stable Pd NPs using five-arm star-shaped block copolymers, with a poly(ethylene oxide) (PEO) core and a poly(ε-caprolactone) (PCL) corona, as templates.[73] The PEO core was swelled with $Pd(OAc)_2$ in *N,N*-dimethyl-formamide (DMF), and Pd NPs were obtained by reduction with $NaBH_4$. Transmission electron microscopy studies strongly suggested that one Pd NP was formed inside each star-shaped block copolymer. The stability of the Pd NPs with respect to aggregation was strongly dependent on the length of the PCL chains.

Many triblock copolymers are commercially available and inexpensive. The PEO*x*–PPO*y*–PEO*x* type, also known as a pluronic copolymer, is widely used as a stabilizing agent because of its low toxicity and amphiphilic nature.[74–78] In the synthesis of Au NPs, pluronic triblock copolymers serve both as reductants and as stabilizers.[74] On the other hand, in the synthesis of Pt NPs, $H_2PtCl_6 \cdot 6H_2O$ was reduced with $NaBH_4$ in the presence of the copolymer as stabilizer.[78]

Polymers were also used as functional supports for NPs.[79] Rhee *et al.* [80] developed the preparation of an amphiphilic PS–PEG [polystyrene–poly(ethylene glycol)] resin-dispersion of Pd NPs. This dispersion catalysed the hydrodechlorination of chloroarenes in water,[81] as well as alcohol autooxidation in water, yielding aldehydes, ketones and carboxylic acids.[82,83] This catalyst combines several features: (1) high catalytic activity; (2) water-based reactivity provided by the amphiphilicity of the PS-PEG matrix; and (3) good filtration and catalyst recyclability.

Dendrimer-Encapsulated Metal Nanoparticles

Dendrimers are monodispersed macromolecules, with a well-defined branched three-dimensional architecture.[84,85] Their structure and chemical properties can be controlled by modifying the core, the type and number of branches, and the terminal functional groups.[79,86] Low-generation dendrimers resemble molecular trees, while high-generation ones are spherical (Fig. 9).[79] The first dendrimer, poly(propyleneimine) (PPI), was synthesized in 1978 by Buleier *et al.*[87] Since then, many new classes of dendrimers have been reported, such as poly(amidoamine) (PAMAM),[88] the arborols of Newkome and co-workers,[89] and the polyether dendrimers described by Piotti *et al.*[90]

Dendrimer-encapsulated nanoparticles (DENPs) are interesting as catalysts for several reasons:[91–93] first, one can control the composition, solubility and immobilization of the NP;[94] second, the dendrimer prevents aggregation, but it does not passivate the active sites on the metal surface; third, DENPs are easily recycled via filtration and centrifugation.[95,96] Finally, the dendrimer can be configured to provide both reactant and product selectivity.[95,97]

DENPs are synthesized by complexing metal ions within dendrimers and then reducing those to zerovalent metal atoms (Fig. 10). The use of DENPs as catalysts was proposed in 1998 by the groups of Crooks[98] and Tomalia.[99] Recent catalytic applications include hydrogenation and C–C coupling in water,[97] organic solvents,[100] biphasic fluorous solvents[95] and supercritical CO_2.[101] Pd DENPs are efficient hydrogenation catalysts. Their activity is related to the density of functional groups on the dendrimer periphery, which is a function of the dendrimer generation.

The properties of the dendrimer are tailored by modifying the terminal groups. For example, the terminal amino groups of PAMAM were protonated at pH 2 prior to complexation by metal ions. The metal ions attached selectively onto the nitrogen atoms, resulting in water solubility of the dendrimer and subsequent catalytic activity in the selective hydrogenation of allylic alcohol and *N*-isopropyl acrylamide in water. Oxidation[102] and reduction[103] catalysis could also be performed by Pd DENPs in PAMAM. Lemo *et al.*[104] found later the same effect for the diaminobutane (DAB) dendrimer for the Suzuki coupling. They derivatised the DAB dendrimer exterior amines by functionalized alkyl chains, increasing the reactivity as well as the recoverability of the Pd DENPs. They also studied the effect of the generation number. In the case of low-generation dendrimers (G1, G2 and G3), the open structure favours the catalytic activity. Conversely, G4 and G5 dendrimers incur lower activity, due to lower substrate accessibility, but also give better Pd encapsulation, and thus less Pd black. Similar effects were reported by Li and El-Sayed *et al.*[105] with PAMAM dendrimers on the catalytic activity of Suzuki cross-coupling. Ooe *et al.*[106] recently reported similar selectivities, based on substrate size and polarity, for Pd DENPs hosted by PPI dendrimers functionalized on the periphery with triethoxybenzamide groups. Specifically, they found that the Pd DENPs showed remarkable selectivity toward polar substrates in the hydrogenation of olefins.

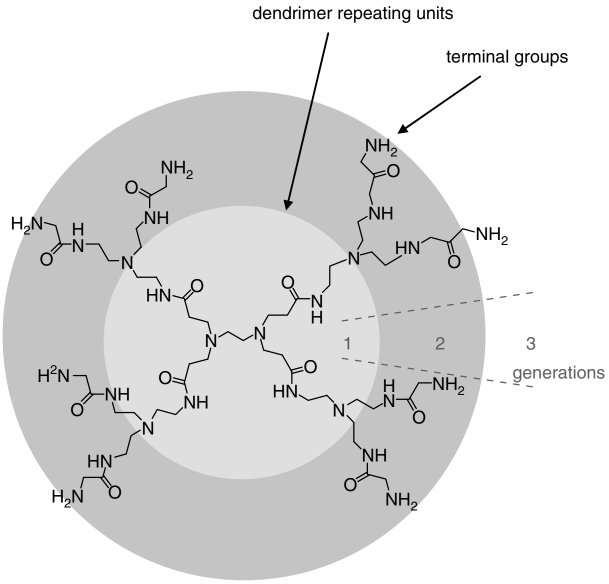

Figure 9. Representation of generational structure PAMAM dendrimer.

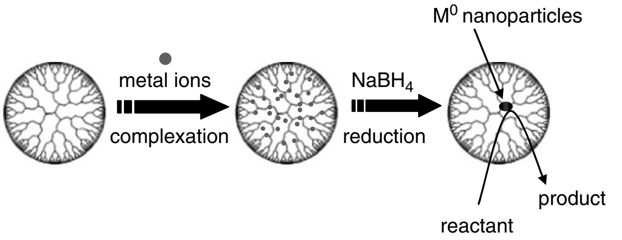

Figure 10. Strategy for stabilizing NPs by PAMAM dendrimers: complexation of a metal cation to the inner nitrogen atoms of tertiary amines, followed by reduction to M^0 by NaBH$_4$, and finally by aggregation that gives the DENPs.

Catalytically active bimetallic DENPs were also reported. Figure 11 shows three different approaches for preparing these materials.[91] The co-complexation route leads to bimetallic alloys, while the other two methods lead either to alloy or core/shell materials, depending on the metals. For example, Pd/Pt alloys can be prepared via the co-complexation route.[107] The resulting Pd/Pt DENPs are water-soluble, stable for over a year in solution, and nearly monodisperse in size (average NP diameter of 1.9 nm). The ratio of the K_2PdCl_4 and K_2PtCl_4 precursors controls the composition. Importantly, TOFs for the hydrogenation of allyl alcohol are significantly higher for the Pd-rich bimetallic DENPs compared with physical mixtures of the single-metal analogues.[107] Chung and Rhee also reported recently synergistic effects for the hydrogenation of cyclohexene by Pd/Pt DENPs[108] and the partial hydrogenation of 1,3-cyclooctadiene by Pd/Rh DENPs.[109]

Core/shell DENPs were also prepared using the sequential dendrimer templating approach illustrated in Fig. 11. For example,

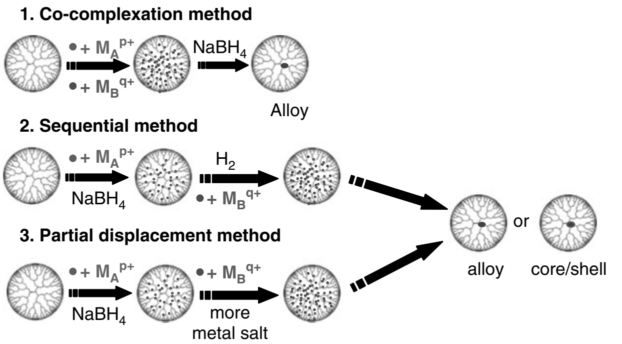

Figure 11. Three possible routes for the synthesis of bimetallic DENPs.[91].

Crooks *et al*. synthesized Au/Pd core/shell NPs, by selectively reducing $PdCl_4$ onto G6-Q116(Au_{55}) seeds using H_2. The average NP size was 1.3 nm. These core/shell catalysts showed superior performance in the hydrogenation of allyl alcohol, compared with homometallic Pd DENPs.[110]

One question that remains open is whether the reduced catalytic activity in higher-generation dendrimers comes from greater resistance to mass transfer imposed on substrates, or a higher percentage of the NP surface being passivated by functional groups. DENPs were used as C–C coupling catalysts.[95,111–114] However, as in many other cases, it is likely that the actual catalysts were atomic/ionic Pd species that leached out from the NPs.[55,56]

Another interesting approach is immobilizing the DENPs on a metallic support. Pt DENPs terminated with hydroxyl functional groups were immobilized on Au surfaces, and used for the electrocatalytic reduction of O_2.[115] DENPs were also incorporated into conducting polymer matrixes, e.g. Pt DENPs using thiophene-terminated PAMAM, and co-electropolymerized within poly (3-methylthiophene).[116] In addition to preparing heterogeneous catalysts from intact DENPs, one can also remove the dendrimer after immobilization. In this case, the only function of the dendrimer is to provide a means of synthesizing the NPs and then dispersing them onto a solid support without agglomeration. Instead of preparing NPs catalysts using preformed DENPs, dendrimers were also used to prepare supported catalysts by calcining dendrimers loaded with metal ions. Removing the dendrimer can improve the catalytic activity, by increasing accessibility to the NP surface. One elegant approach involves incorporating the DENPs into sol–gel matrixes, followed by calcination. This minimizes NP growth, as individual NPs are isolated within the sol–gel framework. Bimetallic DENPs can be also prepared by this sol–gel route.[117] Chandler and co-workers reported the preparation of bimetallic Pt–Cu DENPs in an anaerobic aqueous solution, which were then deposited onto alumina (Fig. 12). The dendrimer template was thermally removed, yielding supported NPs, which were studied as catalysts for toluene hydrogenation and CO oxidation.[118] Jiang and Gao[119] prepared heterogeneous Pd NPs catalysts stabilized by a organic–inorganic hybrid composites, G*n*-PAMAM-SBA-15. These DENPs catalysed the hydrogenation of allyl alcohol. The hydrogenation rate and selectivity were controlled by using different generation dendrimers.

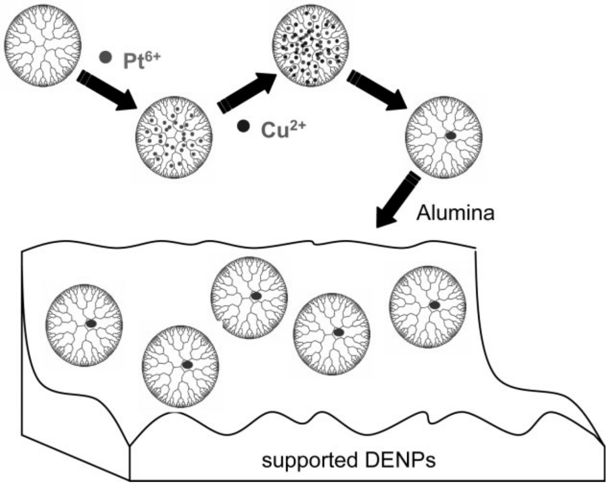

Figure 12. Scheme of preparative route of Cu/Pt DENPs supported on alumina.[118].

NPs in Ionic Liquids

Ionic liquids (ILs) are advancing into many areas of chemistry,[120] and NP catalysts are not exempt.[121–123] ILs are particulary interesting here, as they can function both as stabilizers and as solvents. The list of ILs grows daily, but generally bulky cations favour the electrosteric stabilization of NPs (Fig. 13). These are normally asymmetric ammonium or phosphonium salts, or heteroaromatics, with low symmetry, weak intermolecular interactions and low charge densities.[124]

NPs dispersed in ILs are stable and active catalysts for various reactions such as the hydrogenation of alkenes,[125,126] arenes[127,128] and ketones,[129] hydrodehalogenation of aryl chlorides,[130] and Heck,[131] Suzuki,[132] Stille,[133] Sonogashira[134] and Ullmann[135] coupling reactions. In most of these cases, the reactions are multiphase. The NPs usually form the denser phase, and the substrates and products remain in the lighter phase. The ionic catalytic solution is easily recovered by decantation.[136] Normally, it can be reused several times without any significant loss in catalytic activity, as observed with IL-dispersed Ir, Rh, Pt, Pd and Ru NPs. However, in the case of aromatic compounds and ketones, some metal NPs tend to aggregate.[129] NPs are more stable in the hydrogenation reactions when dispersed in ILs than under solvent-free conditions. Note that aromatics, ketones and alcohols are much more soluble in the ionic media than alkenes and alkanes. Therefore, aromatic and functionalized compounds are likely to 'wash out' the protective ionic liquid species from the metal surface, thereby facilitating the aggregation.

Interestingly, adding a co-stabilizer such as an ionic copolymer[137] or PVP[68] can increase the NP stability and the activity performance. Huang *et al*.[138] immobilized Pd NPs onto molecular sieves using 1,1,3,3-tetramethylguanidinium lactate. These NPs were very active and stable olefin hydrogenation catalysts.

Another highly interesting approach is placing ligands on the metal surface. Pd NPs in 'classical' ILs such as BMI · PF_6, tend to agglomerate after the hydrogenation of alkenes.[139] However, phenanthroline-protected Pd NPs in this IL are very active and selective in olefin hydrogenation, and the NP–IL system can be reused several times without losing activity.[140] Fernández *et al*.[141] showed that the presence of hydroxyl groups in amine ligands enhances the stability of the Pd NPs in BMI · PF_6. TEM analyses after catalysis show the formation of small NPs in contrast to the agglomerates observed when using preformed NPs. The latter also showed a lower catalytic activity. Poison tests reveal that Pd^0 is involved in the catalytic processes.

Moreover, investigations by Dyson and co-workers on functionalized ILs, such as imidazolium or pyridinium salts with the nitrile functional group attached to the alkyl side, demonstrated that ILs can be both solvent and ligand for metal-catalysed reactions.[142] For example, Pd NPs immobilized in both *N*-butylpyridinium and nitrile-functionalized ILs showed good catalytic activity for Suzuki,

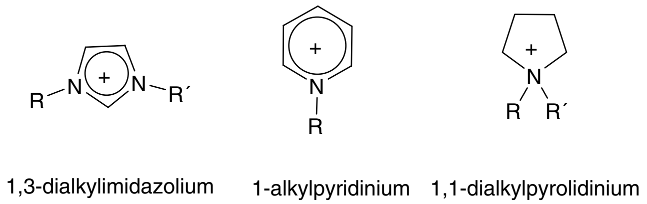

Figure 13. Some of the common cations used for making room-temperature ionic liquids.

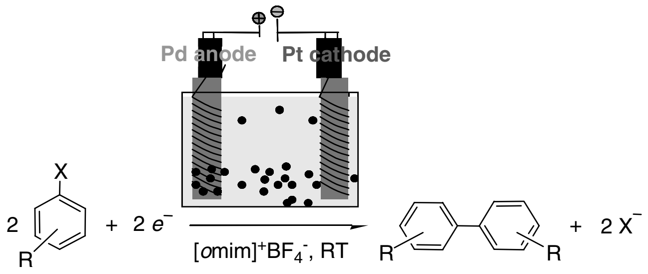

Figure 14. Pd NPs catalysed electroreductive homocoupling of organic halides in IL.[135,146].

Heck and Stille coupling reactions, but recycling and reuse is simpler in the nitrile-functionalized IL.[143,144] Recently, Abu-Reziq *et al.*[145] reported a method for supporting Pt NPs on magnetite NPs modifided by ILs. This material catalysed the selective hydrogenation of alkynes to alkenes, and α,β-unsuturated aldehydes to allyl alcohols. The solid catalyst was easily separated and recycled by applying an external magnetic field.

We reported in 2006 a catalytic alternative to the Ullmann reaction based on reductive homocoupling catalysed by Pd NPs in [octylmethylimidazolium]$^+$[BF$_4$]$^-$ (used as stabilizer, solvent and electrolyte).[135,146] The particles were generated *in situ* in an electrochemical cell. Spherical well-dispersed particles were obtained (2.5 ± 0.5 nm). This reaction system requires only aryl halide, electricity and water (Fig. 14). The kinetics of the reaction for PhI coupling were monitored and an induction period of almost 3 h was observed. This induction period supports the involvement of Pd clusters in the cycle.

Metal NPs dispersed in ILs can also tune the selectivity of the reaction by using multiphase catalytic processes. In these systems, the products are extracted during the reaction. For example, 1,3-butadiene is at least four times more soluble in BMI · BF$_4$ than butanes. Therefore, the selective partial hydrogenation could be performed by Pd NPs embedded in the ILs (selectivities up to 72% in 1-butene were achieved at 99% 1,3-butadiene conversion). Similarly, the solubility difference of benzene and cyclohexene (a maximum of 1% cyclohexene concentration is attained at 4% of benzene concentration in BMI·PF$_6$) was used for the hydrogenation of benzene to cyclohexene with a 39% selectivity at low benzene conversions by Ru NPs dispersed in BMI · PF$_6$.[147]

NPs Stabilized by Surfactants, Micelles and Microemulsions

The first surfactant-stabilized NP suspensions were reported in 1976 by Lisichkin *et al.*[148] and in 1979 by Kiwi and Gritzel.[149] The surfactants prevent undesired agglomeration by forming a monomolecular layer around the metal core. Lipophilic surfactants of tile cationic type such as tetraalkylammonium halides (R$_4$N$^+$X$^-$) can give very stable NP organosols.[150] This kind of Pd NPs was prepared size-selectively (1–5 nm) in organic solvents or in water, by reducing chemically a Pd salt such as PdCl$_2$, Pd(OAc)$_2$ or Pd(NO$_3$)$_2$ in the presence of a tetraalkyl ammonium salts.[151,152]

In 1999, Reetz and Maase[153] discovered that an external reducing agent is not necessary if the Pd precursor is gently warmed in organic solvents in the presence of excess tetraalkylammonium carboxylates. The NPs (l–10 nm in size) are well protected from agglomeration by a monolayer of the long-chain alkyl groups.[151] Tetraalkylammonium-stabilized NPs were used as catalysts in various reactions, including hydrosilation, oxidation, C–C coupling, hydrogenations and cycloadditions.[21,154] Recently, Singla *et al.*[155] reported the synthesis of monodisperse pure Ni NPs in water using CTAB and a mixture of TEAB and TBAB. The particles (∼15 nm spheres) were stable in air up to 325 °C and catalysed the reduction of *p*-nitrophenol in the presence of hydrazine hydrate as reducing agent.

By this method, bimetallic Cu–Pd NPs were also prepared. The idea behind was that mixing two or more metal precursors led to synergistic effects that improved the catalytic activity. In fact, Cu–Pd NPs showed better catalytic activity than Cu or Pd NPs in Suzuki cross-coupling. Reetz *et al.* reported previously the synthesis of bimetallic NPs with TOAF: Pd–Pt (2.2 nm), Pd–Sn (4.4 nm), Pd–Au (3.3 nm), Pd–Rh (1.8 nm), Pt–Ru (1.7 nm) and Pd–Cu (2.2 nm). The advantages of this redox controlled method is that it requires no complicated separation or purification procedures, and the NPs can be redispersed in polar solvents.

We presented also the synthesis of core/shell Ni–Pd NPs, and their application as Hiyama coupling catalysts (Fig. 15).[38] The preparation combined electrochemical and 'wet chemical' techniques, giving highly monodispersed structured bimetallic NPs (4.9 nm mean diameter, see Fig. 16). In this way, no Pd is 'wasted' in the NP cores. The core/shell NPs were superior catalysts compared with the Ni–Pd alloy, and to Pd or Ni monometallic ones.

In the 1990s, the stabilization of NPs by micelles and their application in catalysis was intensively investigated.[156–159] Mayer and Mark[160] reported the preparation of NPs in the micellar corona of polystyrene–block–poly(ethylene oxide) and polystyrene–block–poly(methacrylic acid) with a polystyrene core and their activity in cyclohexene hydrogenation. Seregina *et al.*[161] developed monometallic and bimetallic NPs stabilized in the micellar core of polystyrene–block–poly-4-vinylpyridine

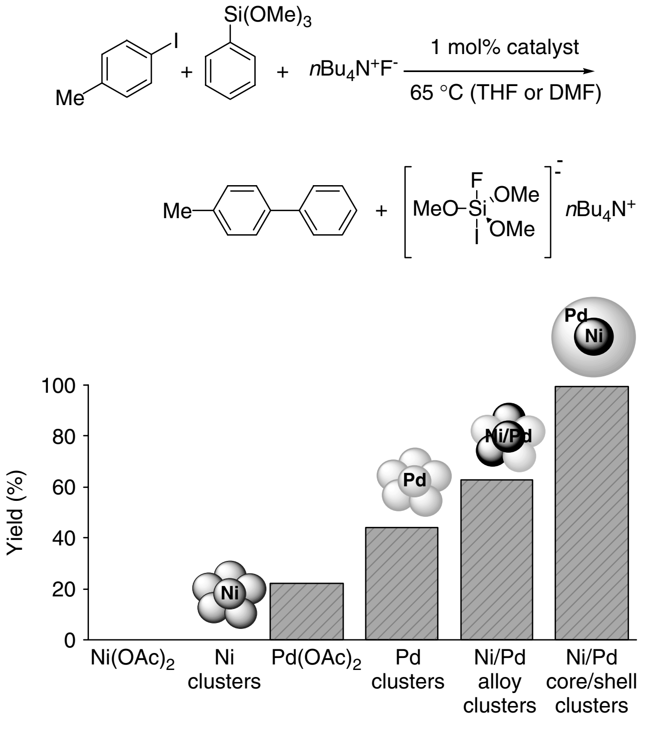

Figure 15. Ni/Pd core/shell NPs catalysed Hiyama cross-coupling (top) and comparison of the catalytic activity for six different systems in the Hiyama coupling (bottom).[38].

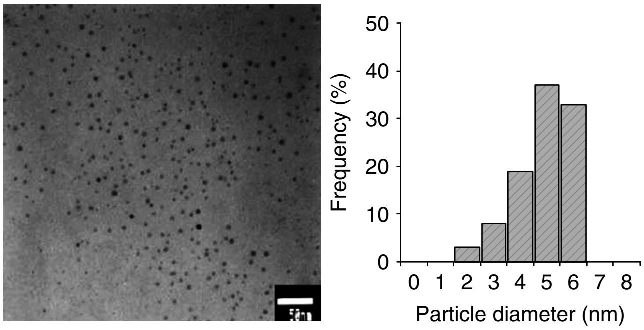

Figure 16. Transmission electron micrograph (left, magnification ×200, 000) and corresponding size distribution (right, based on 100 particles counted) of the core/shell Ni/Pd NPs.

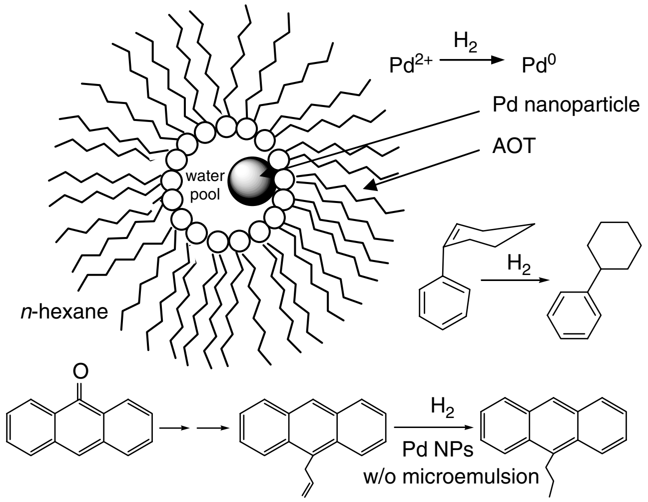

Figure 17. Hydrogenation of anthracene catalysed by Pd NPs in w/o microemulsions.

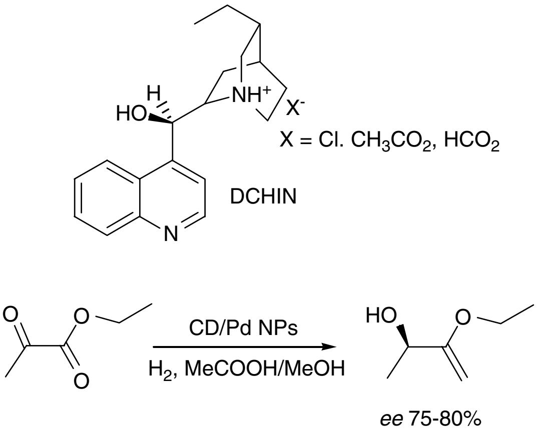

Figure 18. Enantioselective hydrogenation of ethyl pyruvate catalysed by CD-Pt NPs or CD-Pd NPs.

(PS-*b*-P4VP) in toluene for hydrogenations. One drawback of micelle-stabilized NPs is their difficult separation from the reaction products. This can be solved by ultrafiltration,[157] or by using $scCO_2$.[158] Tsang *et al.*[162] reported catalytic hydrogenation of citral by micelle-hosted Pd NPs in $scCO_2$. The molecular orientation of citral, guided by the micelle assemblies, allows a highly selective hydrogenation of the α,β-conjugated double bond that is near to the Pd surface. Micelle-hosted bimetallic NPs were also reported. For example, Pd–Ru NPs in reverse micelles with for catalytic selective hydrogenation of alkenes in $scCO_2$.[163] In these systems, H_2 was the reducing agent both for the Pd salts and for the unsaturated substrate.

Another interesting method for producing monodispersed NPs is synthesis in water-containing reverse micelles or microemulsions. Boutonnet *et al.*[164] first used aqueous pools of w/o microemulsions to solubilize simple ionic metal salts of Au, Pd, Pt and Rh, followed by chemical reduction using N_2H_4 or H_2.[165] Pileni and coworkers employed a anionic inverse microemulsion system to control the growth and stabilization of the NPs (Fig. 17).[166–168] The inverse microemulsion synthesis is used as an NP size control by the water-to-surfactant ratio. The growth of the micelle water pool is restricted by the pool size, and the NP is stabilized by a shell of surfactant molecules. One limitation of using water-containing microemulsions is the limited number of suitable reducing agents, basically N_2H_4 or $NaBH_4$.

Ligand-Stabilized NPs

The introduction of ligands as NP stabilizers is of special interest, because it enables the creation of an asymmetric environment. The first example of enantioselective catalysis by NPs was reported in 1994 by Nasar *et al.*[169] They showed that Rh NPs catalysed hydrogenations of disubstituted aromatic rings induced by a chiral amine, *R*-dioctylcyclohexyl-1-ethylamine as ligand. Bönnemann and co-workers reported the efficiently catalysed hydrogenation of ethyl pyruvate by Pt or Pd NPs with cinchonidine ligands (up to 95–98% *ee*, see Fig. 18).[170,171] Fujihara and co-workers reported 2,2′-bis(diphenylphosphino)-1,1′-binaphtyl (BINAP)-stabilized Pd NPs (2.0 ± 0.5 nm of diameter).[172] These BINAP–Pd NPs catalysed the asymmetric hydrosilylation of styrene under mild conditions (95% *ee*), whereas mononuclear BINAP–Pd complexes were inactive. Chaudret and co-wokers also reported enantioselective allylic alkylation reactions, with up to 97% *ee*, that were catalysed by Pd NPs stabilized by a chiral xylofuranide diphosphite.[173] In the above-mentioned reports it is suggested that the NPs 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.

Pd NPs stabilized with special ligands, such as polyoxometallates[174] and cyclodextrins[175] were also active as catalysts in the hydrogenation of unsaturated substrates and in the Suzuki, Heck and Stille reactions. For example, perthiolated β-cyclodextrin-Pd NPs catalysed the coupling of iodo and bromoarenes and iodoferrocene with phenyl boronic acid in $MeCN/H_2O$. These 3 nm Pd NPs also catalysed the hydrogenation of alkenes in water.[175]

Thiol chemistry was extensively employed for attaching different functionalities as ligands and for synthesizing NPs.[176–178] Recently, Ananikov *et al.*[179] reported the synthesis of Pd NP using alkynethiol as a stabilizing ligand. Note that the range of metals for which thiol-NPs can be prepared is limited by the stability of the metal–sulfur bond. Schiffrin and co-workers[180] proposed a new route to Au and Pt NPs via metal–carbon bonds. The synthesis is based on the reduction of the diazonium salt derivative of a long-chain alkyl benzene that acts both as a phase-transfer reagent and as a stabilizing ligand. Another simple mode of stabilization involves adding silanes, such as *tert*-butyldimethylsilane, to $PdCl_2$ or $Pd(OAc)_2$. The NPs formed catalysed the selective cross-coupling of the silane with phenyl and vinyl thioethers, giving the corresponding thiosilanes and silthianes.[181]

NPs Supported on Metal Oxides or Carbon Supports

Immobilizing NPs on solid supports can minimize atom/ion leaching from the particles. Recent reports focused on the catalytic properties of NPs supported on metal oxides.[182] The metals are from Si,[183] Al,[184] Ti[185] or Zr[186] to Ca,[187] Mg[188] and Zn[189]. The majority of them, and the most extensively used, contain a form of silica. These oxides take various forms, such as SiO_2 sol–gels,[190] silica spheres,[191] silica microemulsions,[192] molecular sieves[193] and zeolites.[194] The catalytic reactions examined are selective hydrogenation reactions 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 support such as silica brings the classic advantages of heterogeneous catalysis. Pt NPs and bimetallic dendrimer-stabilized Pd–Au NPs were adsorbed onto a high-surface silica support and thermally activated to remove the dendrimers. The Chandler group showed that these NPs were smaller than 3 nm and highly active for CO oxidation at 25 °C.[183]

Immobilization of micellar NPs was reported by Semagina *et al*.[195] They prepared Pd NPs stabilized in micellar core of poly(ethylene oxide)–block–poly-2-vinylpyridine (PEO-*b*-P2VP) and applied and supported on γ-alumina. The material was applied as a highly selective and active catalyst for the 2-butyne-1,4- diol partial hydrogenation. The supported catalyst was reused several times, showing the Pd NPs' stability inside the micellar core. However, the supported catalyst showed some micelle desorption (<5% during reaction run) from the alumina. Studies found an inhibiting effect of surfactants on the NPs. Removing the surfactant after the micelle immobilization increases the catalytic activity, but the main advantage of micellar catalysis, i.e., the improved catalytic performance due to the specific medium, is lost.[157]

Das *et al*.[196] synthesized mono-dispersed supported Pd NPs on MCM-41. The pores were expanded by post-synthesis treatment with *N*,*N*-dimethyldecylamine. The NPs were prepared at 25 °C, but showed good thermal stability – their size increased from 2.8 to only 3.4 nm after calcination at 500 °C. They catalysed Suzuki coupling reactions, with practically no leaching. The leaching was tested by interrupting the reaction at 60% conversion, followed by separating the catalyst and monitoring the filtrate for an extended period. No appreciable change in conversion was noted. A hot filtration test was carried out at 78 °C. Fresh substrates were added to the filtrate but no further conversion was observed. ICP analysis of the filtrate showed only 6 ppb of Pd.

NPs were also impregnated on carbon supports. Activated carbons that are suitable as support materials in catalytic processes need to be prepared and modified to get the desired surface area, porosity and pore size distribution. Bönnemann developed a general synthetic method where the carbon is impregnated by simply stirring in the NP suspension.[197] Reetz *et al*. used this method to support their electrochemically prepared metal NPs including catalytically active bimetallic NPs.[198] Typical catalytic applications for these materials are hydrogenation reactions and also Suzuki and other C–C forming reactions.[199–201] The mechanism is quasi-homogeneous, and small Pd species in solution act as the catalytically active species. The Pd is leached and, at the end of the reaction redeposited, enabling recovery of the precious metal from the reaction mixture. At the end of the reaction the catalyst precipitates. Kohler *et al*.[202] showed that the efficiency of the Pd–C catalyst strongly depends on the Pd dispersion, oxidation state in the fresh catalyst, impregnation method and pre-treatment. High-area carbon was used to prepare bimetallic Pt–RuNPs that catalyse methanol electrooxidation with enhanced activities compared with commercial catalysts.[203]

Ni NPs on carbon were used as catalysts for hydrogenating unsaturated compounds,[204] hydrodehalogenation of aryl halides,[205] Kumada,[206] Suzuki[207] and Negishi-type C–C coupling[208] and aromatic amination.[209] However, the C–C and C–N coupling reactions showed that Ni leached from the support during the reaction, re-adsorbing at the end of the reaction.

Recently, Su *et al*.[210] reported a simple thermal reduction method for preparing Ru NPs supported on mesoporous SBA silica, surface-carbon-coated SBA or templated mesoporous carbon. The Ru NPs exhibited good dispersion and resistance against oxidation, lack of aggregation and pore blocking, and less leaching. These NPs showed higher catalytic activity and stability in hydrogenation of benzene and toluene compared with the NPs prepared by traditional methods.

Conclusions and Future Perspectives

Big steps have been made in NP synthesis in the last decade. There are reproducible methods for making structured NPs, with good control over size, shape and composition. In this respect, NPs may yet fulfill the promises of nanotechnology with regard to bottom-up synthesis and device manufacturing.

As far as catalysis is concerned, the situation is less promising. Often, the NP suspension is simply a reservoir for metal atoms/ions that leach into solution. This leaching is now proven for several types of NP suspensions in various reactions, especially for the catalycally active group VIII transition metals. Because of this, researchers reporting NP catalysis must henceforth also convince their readers that the NPs are the true catalysts. This can be done using hot filtration experiments, combined with UV/IR spectroscopy and ICP analysis.

Currently, there are three promising approaches for dealing with the leaching problem: the first is by immobilizing the NPs on a solid surface. This cuts down the leaching, but also reduces substrate accessibility. Alternatively, biphasic separation using ILs can minimize leaching while still keeping the NPs accessible. Finally, there is the 'if you can't beat them – join them' tactic: using NP suspensions knowing that leaching occurs, and thereby maintaining in solution a low concentration of very active homogeneous ligand-free catalysts. The de Vries group at DSM has recently demonstated this approach for Pd-catalysed Heck reactions.[52]

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