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Reduced Transition Metal Colloids: A Novel Family of Reusable Catalysts?

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I. Introduction

The word "colloid" was introduced for the first time by Graham in 1861[1] to describe the very slow sedimentation and noncrystalline state, two characteristic appearances of aqueous solution made of compounds well-known to be insoluble in water such as silver or gold chloride. In its starting definition, this term implied the suspension of a phase (solid or liquid) into a second phase, and was used for suspensions, which neither settled nor deposited spontaneously. These properties have led Graham to postulate that these colloidal particles should be large enough (above 1 nm) and of relatively weak size in order not to settle out (below 1 μm).

There are, in this way, very different types of colloids according to the physical phase of dispersed compounds and the environment of dispersion. The term "colloid" brings together a great diversity of compounds such as polymer suspensions in solution, emulsions constituted by amphiphilic molecules in aqueous or organic mixture, and finally dispersions of inorganic particles. For long time, the properties of inorganic colloids and more precisely metal nanoparticles have interested scientists.[2−5] This interest is mainly due to their aesthetic properties as pigments in ceramics or their technological properties as catalysis. During the 20th Century, substantial progress has been obtained in the synthesis of metal colloids. Ostwald and Turkevitch[6] works have thus allowed understanding better the nucleation processes, growing and agglomeration linked up to the preparation of metal nanoparticles.

Recently, several criteria have been summarized by Finke to distinguish modern nanoclusters from traditional colloids such as the control over the composition, size, surface-ligating anions and other ligands, and finally the control over the desired properties: solubility in an appropriate solvent, isolability, and redissolvability.[7] Additional kinetic and mechanistic studies in modern transition metal nanoclusters formation have also been performed, and, finally, a novel mechanism consisting of slow continuous nucleation followed by fast autocatalytic surface growth leading to near-monodispersed nanoclusters has been proposed.[8−10]

Now, essential challenges must be taken up: (i) finding new and reproducible methods of synthesis allowing stable and monodispersed suspensions of metal colloids which have a size between 1 and 10

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Alain Roucoux was born in Valenciennes (North of France) in 1963. He graduated from the University of Lille and received his Ph.D degree in 1992 under the direction of A. Mortreux for work on asymmetric hydrogenation of ketones. In 1993, he obtained a permanent position ≪ Maître de Conférences ≫ at the Ecole Nationale Supérieure de Chimie de Rennes and joined the group of H. Patin to develop water-soluble complexes for carbon–carbon bond formation in biphasic media. His recent research topics include the synthesis of stabilized transition metal nanoparticles and their application in catalysis including hydrogenation and oxidation.

Jürgen Schulz was born in Antibes, France, in 1973. He graduated from Ecole Nationale Supérieure de Chimie de Rennes in 1996. He received his Ph.D. degree from the University of Rennes in 2000 for studies concerning the use of transition metal nanoparticles as catalysts in biphasic (water/organic) media under the co-direction of Professor H. Patin and Dr A. Roucoux. Since 2001, he joined the group of Professor M. Lemaire to perform an industrial postdoctoral position for Total Fina Elf concerning the deep desulfurization of gasoil with organic molecules. His other research interests lie in heterogeneization of catalysts and organic materials.

Professor Henri Patin studied chemistry at the University of Rennes where he obtained his Ph.D. in 1969 with a thesis on reactivity and stereochemical aspects of ferrocene and other metallocenes. After a Doctorate ès Sciences in 1972 with new developments in organotin chemistry, he turned to general organometallic chemistry with emphasis on homogeneous catalysis. He was a research associate in the team of Sir Derek Barton at Imperial College London from 1974 to 1976 developing new reactions useful in organic synthesis. Back in France, he designed new strategies for the synthesis of clusters of Fe, Co, Mo in view of catalytic applications and published the first paper on electron-transfer catalysis applied to control of ligand exchanges in polynuclear complexes. In 1984, he was appointed Professor at ENSCR (École Nationale Supérieure de Chimie de Rennes) and head of the Chemistry Department. In this School of Engineers, he started fruitful collaborations with industries in the fields of biphasic catalysis (hydrophilic ligands and complexes) and more fundamental aspects of biocatalysis (desaturases). From 1991 to 2001, he was Director of ENSCR; he continued research in these fields and opened new axes with radiopharmaceuticals (Tc, Re) and design of amphiphilic compounds for pharmaceutical applications. He is now Director of Industrial Relationships at ENSCR and Head of the Laboratory of Chemistry of Biomolecules and Organised Systems. He is also involved in technology transfer and creations of start-up. Professor Henri Patin is author and coauthor of some 170 papers and 10 patents. His interest in colloïdal metals arose some 15 years ago when he discovered the oxydo-reduction in water between rhodium (III) and TPPTS leading to an efficient and reusable colloïdal mixture able to perform hydrogenation of alkenes in very smooth conditions.

nm, (ii) using new methods of characterization to elucidate the microstructures of these nanoparticles, and (iii) developing new applications. However, supplementary key research goals in modern nanoclusters science can be proposed as previously reported.[7]

Today, catalysis is the essential application of metal nanoparticles, but they find also application in such diverse fields as photochemistry, nanoelectronics, or optics.[11−18] As catalysts, these systems show a great potential because of the large surface area of the particles. Many chemists suggest that metal colloids are very efficient catalysts because of a great ratio of atoms remaining at the surface, and so available to chemical transformation of substrates. In fact, these catalysts are microheterogeneous systems bearing metal nanoparticles. Undoubtedly, many catalytic transformations have been carried out with microheterogeneous metal catalysts while chemists believed that they were performed by homogeneous catalysts.[19−22] Since that time, modern methods to distinguish homogeneous from heterogeneous catalysts were described.[23−24]

The original catalytic approach is to use colloidal metallic particles finely dispersed in organic or aqueous solution or a solvent mixture. Generally, these suspensions must be stabilized by protective agents to prevent aggregation and/or to facilitate recycling. One disadvantage of soluble colloidal metals is the recovery of the catalyst from the reaction products. This can be overcomed by using aqueous/organic biphasic conditions or other immobilization systems such as, for instance, fluorinated solvents or thin films of liquids on porous supports.

This review covers the different methods of metal nanoparticles synthesis including the stabilization of microheterogeneous systems. Finally, the catalytic applications will be cited, and more precisely those that have the most important impact at industrial and academic level. We will mention the most promising systems with regards to the reusable abilities.

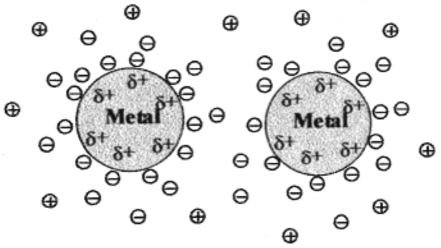


Figure 1. Schematic representation of electrostatic stabilization of metal colloid particles.

II. Formation of Transition Metal Colloids

II.1. Stabilization of Colloids

One of the main characteristics of colloidal particles is their small size. Unfortunately, these metallic nanoparticles are unstable with respect to agglomeration to the bulk. In most cases, this aggregation leads to the loss of the properties associated with the colloidal state of these metallic particles. For example, during catalysis the coagulation of colloidal particles used as catalyst leads to a significant loss of activity. The stabilization of metallic colloids and thus the means to preserve their finely dispersed state is a crucial aspect to consider during their synthesis. Several general discussions on the stability of colloids and nanoclusters have been already reported.[7,13,24−31]

At short interparticle distances, the van der Waals forces will attract two metallic particles to each other. These forces vary inversely as the sixth power of the distance between their surfaces. In the absence of repulsive forces opposed to the van der Waals forces, the colloidal metal particles will aggregate. Consequently, the use of a stabilizing agent able to induce a repulsive force opposed to the van der Waals forces is necessary to provide stable nanoparticles in solution.[32]

The general stabilization mechanisms of colloidal materials have been described in Derjaguin-Landau-Verwey-Overbeek (DLVO) theory.[33] Nanocluster stabilization is usually discussed in terms of two general categories: (i) charge stabilization and (ii) steric stabilization.

In the present review, based on the stabilizing agents used, we suggest to distinguish four kinds of stabilization procedures: (i) the electrostatic stabilization by the surface adsorbed anions, (ii) the steric stabilization by the presence of bulky groups, (iii) the combination of these two kinds of stabilization with the electrosteric stabilization such as surfactants, and finally (iv) the stabilization with a ligand.

II.1.1. Electrostatic Stabilization

Ionic compounds such as halides, carboxylates, or polyoxoanions, dissolved in (generally aqueous) solution can generate the electrostatic stabilization. The adsorption of these compounds and their related counterions on the metallic surface will generate an electrical double-layer around the particles (Figure 1). This results in a Coulombic repulsion between the particles. If the electric potential associated with the double layer is high enough, then the electrostatic repulsion will prevent particle aggregation.[7,13,28,34]

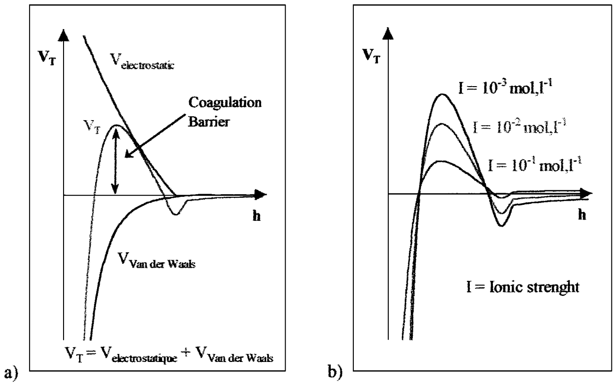


Figure 2. (a) Plot of energy (V_T) vs interparticular distance (h) for electrostatic stabilization. (b) Influence of the ionic strength.

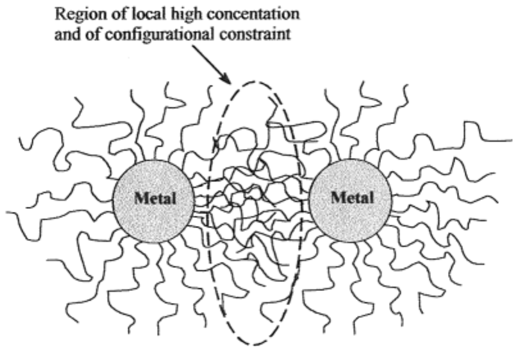


Figure 3. Schematic representation of steric stabilization of metal colloid particles.

Colloidal suspensions stabilized by electrostatic repulsion are very sensitive to any phenomenon able to disrupt the double layer like ionic strength or thermal motion (Figure 2). So the control of these parameters is essential to guarantee an effective electrostatic stabilization.

II.1.2. Steric Stabilization

A second means by which metal colloids can be prevented from aggregating is to use macromolecules such as polymers or oligomers.[28,35] The adsorption of these molecules at the surfaces of the particles will provide a protective layer. The way in which these large adsorbed molecules prevent aggregation can be explained in a simplified manner by visualizing the approach of two metallic colloids. In the interparticle space, adsorbed molecules will be restricted in motion, which causes a decrease in entropy and thus an increase in free energy (Figure 3).

A second effect is due to the local increase in concentration of adsorbed macromolecules as the two protective layers begin to interpenetrate. This result in an osmotic repulsion as the solvent will reestablish the equilibrium by diluting the macromolecules and thus separating the particles. The variation of potential energy versus interparticle distance is shown in Figure 4.

By contrast with the electrostatic stabilization, which is mainly used in aqueous media, the steric stabilization can be used in organic or in aqueous

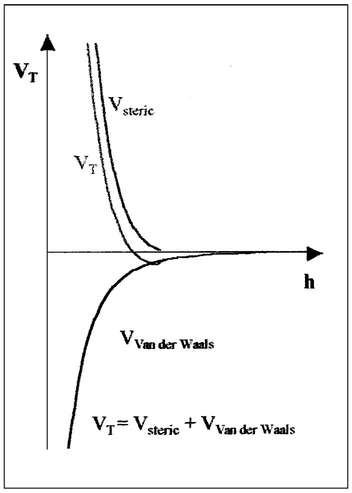


Figure 4. Plot of energy (V_T) vs interparticular distance (*h*) for electrostatic stabilization.

phase. Nevertheless, the length and/or the nature of the macromolecules adsorbed influence the thickness of the protective layer and can thus modify the stability of the colloidal metal particles.

II.1.3. Electrosteric Stabilization

The electrostatic and steric stabilization can be combined to maintain metallic nanoparticles stable in solution.[24,36] This kind of stabilization is generally provided by means of ionic surfactants. These compounds bear a polar headgroup able to generate an electric double layer and a lypophilic side chain able to provide steric repulsion. The electrosteric stabilization can be also obtained from polyoxoanions such as the couple ammonium (Bu_4N^+)/polyoxoanion ($P_2W_{15}Nb_3O_{62}{}^{9-}$). The significant steric repulsion of the associated bulky Bu_4N^+ countercations associated with the highly charged polyoxoanion (Coulombic repulsion) provide an efficient electrosterical stability toward agglomeration in solution of the resultant nanoclusters.[13,36] The variation of potential energy versus interparticle distance is shown in Figure 5.

II.1.4. Stabilization by a Ligand or a Solvent

The term *ligand stabilization* has been chosen to describe the use of traditional ligands to stabilize transition metal colloids. This stabilization occurs by the coordination of metallic nanoparticles with ligands such as phosphines,[37−39] thiols,[40,41] amines,[42−44] or carbon monoxide.[45] For example, Schmid and coworkers synthesized Au, Pt, Pd, and Ni colloids stabilized by phosphines.[37−39] The phenanthroline and its derivatives[42−44] and octanthiol[40,41] have also been used to prepare Pt and Pd colloids.

It has recently been reported that nanoparticles can be stabilized only by solvent molecules. Thus, Ti[46−50] and Ru[51] nanoparticles were synthesized in tetrahydrofuran or thioethers without adding steric or electrostatic stabilizers. However, in both cases, it has not been established that there is no coordination of the heteroatoms of the solvents with the metallic surface. Moreover, proof of the absence of stabilizing agents such as anions or cations is lacking. Sometimes, elemental analysis shows that potentially coordinating bromide or chloride anions still remain.[50]

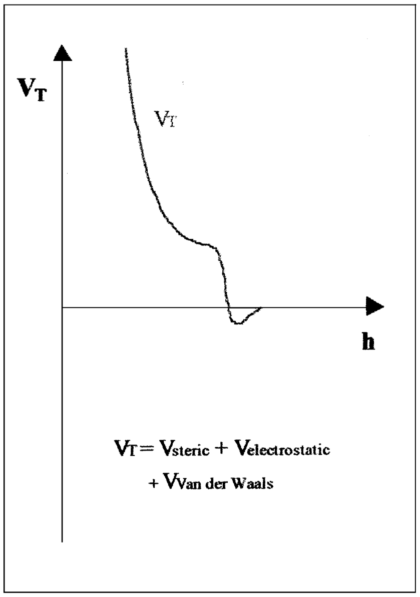


Figure 5. Plot of energy (V_T) vs interparticular distance (*h*) for electrosteric stabilization.

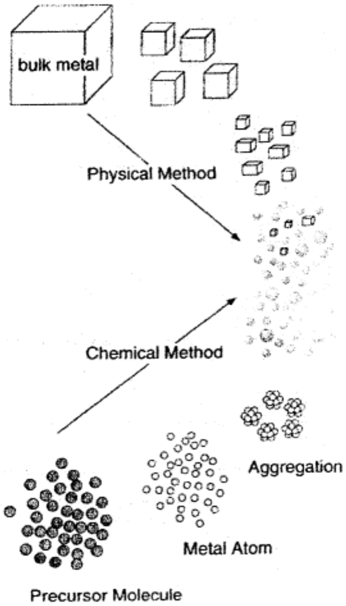


Figure 6. Schematic illustration of preparative methods of metal nanoparticles (Reprinted from ref 250).

II.2. Synthesis of Metal Nanoparticles

Dispersions of metallic nanoparticles can be obtained by two main methods (Figure 6): (i) mechanic subdivision of metallic aggregates (physical method) or (ii) nucleation and growth of metallic atoms (chemical method).

The physical methods yield dispersions where the particle size distribution is very broad. Traditional colloids are typically larger (>10 nm) and not reproducibly prepared giving irreproducible catalytic activity.[52] Chemical methods such as the reduction of transition metal salts are the most convenient ways to control the size of the particles. Today, the key goal in the transition metal colloid area is the development of reproducible nanoparticles (or modern nanoclusters) syntheses in opposition to traditional colloids. As previously reported nanoclusters should be or have at least (i) specific size (1−10 nm), (ii) well-defined surface composition, (iii) reproducible synthesis and properties, and (iv) isolable and redissolvable (“Bottleable”).[7]

Here, we have chosen to review exclusively the chemical methods involved.

II.2.1. Preparation of Colloids Dispersed in a Liquid Media

Colloidal suspensions can be obtained by various methods leading to various particles size distributions. Nevertheless, whatever the method used a stabilizing agent is always necessary to prevent the aggregation of the colloids formed into larger particles.

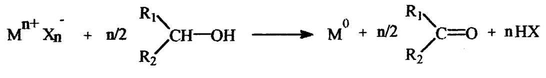
Five general synthetic methods are mainly used in the literature to synthesize transition metal colloids: (i) chemical reduction of transition metal salts, (ii) thermal, photochemical, or sonochemical decomposition, (iii) ligand reduction and displacement from organometallics, (iv) metal vapor synthesis, and (iv) electrochemical reduction.

II.2.1.1. Chemical Reduction of Metal Salts. The reduction of transition metal salts in solution is the most widely used method to generate colloidal suspensions of metals. In fact, this method is generally very simple to implement.

A wide range of reducing agents have been used to obtain colloidal materials: gas such as hydrogen or carbon monoxide, hydrides or salts such as sodium borohydride or sodium citrate, or even oxidable solvents such as alcohols.

II.2.1.1.1. Alcohols. Some transition metal salts can be reduced in refluxing alcohol. In this process, the alcohol acts both as solvent and reducing agent. Generally, the alcohols, which are useful reducing agents, contain α-hydrogen. Thus, methanol, ethanol, or 2-propanol are good reducing agents, whereas *tert*-butyl alcohol is not effective. During the reduction, the alcohols are oxidized to the corresponding carbonyl compounds (Scheme 1). This reaction often requires the presence of water to be effective.

Scheme 1. Formation of Metallic Nanoparticles in Alcoholic Media



$$M^{n+}X_n^- + n/2\ R_1R_2CH{-}OH \longrightarrow M^0 + n/2\ R_1R_2C{=}O + nHX$$

Hirai or more recently Delmas have extensively used aqueous alcohols as reducing agents in the synthesis of colloidal transition metals such as Rh, Pt, Pd, Os, or Ir. All these colloidal suspensions were stabilized by organic polymers or oligomers such as polyvinylic alcohol (PVA), polyvinylpyrrolidinone (PVP), polyvinylic ether (PVE), or cyclodextrine.[53−60] Other kinds of polymers were used for the stabilization of colloids formed during the metallic salt reduction. The use of various polyacides,[61−64] polyelectrolytes,[61,62,65] or block copolymers[61,62,67,68] to stabilize Pd, Pt, and Au[66] nanoparticles has been largely studied. In the same way, after reduction in aqueous alcohol Pt colloids were stabilized by poly(*N*-isopropylacrylamide) (PNIPAAm),[69−72] poly(*N*-sulfonatopropyl-*p*-benzamide),[73] or PVA/PVP copolymers.[74]

Recently, several groups investigated the influence of various parameters on the particle size distribution of the particles synthesized. The variation of stabilizing agent quantity,[75−79] structure and quantity of alcohol,[75−79] metallic precursor,[78,79] as well as the addition of base[80] were studied. For example, the reduction of H_2PdCl_4,[75] H_2PtCl_6,[76] or $RhCl_3$[77] leads to smaller particles when the alcohol used had a higher boiling point. In the same way, the addition of NaOH during the reduction of H_2PtCl_6 or $PdCl_2$ with methanol allows a decreasing of the size of the particles formed.[80] The effects of heating were as well studied.[81] In fact, the quick heating by microwaves of an aqueous alcoholic solution of H_2PtCl_6 allows the production of nearly monodispersed Pt nanoparticles.

II.2.1.1.2. Hydrogen and Carbon Monoxide. Hydrogen is one of the most widely used reducing agents to prepare transition metal nanoparticles. Aqueous colloidal solutions of Au, Ag, Ir, Pt, Pd, Rh, or Ru stabilized by PVA were prepared by hydrogen reduction of the corresponding choride salts.[82] Other organic polymers were used to stabilize metallic colloids. Accordingly, hydrazine polyacrilic acid stabilizes Pt nanoparticles.[83]

Boutonnet[84,85]used hydrogen reduction to generate various transition metal nanoparticles in microemulsions. This method allows the formation of Rh, Pt, Pd, and Ir colloids.

In our laboratory, Rh nanoparticles were synthesized[86,87] by hydrogen reduction of an aqueous solution of $RhCl_3$ in the presence of a trisulfonated surfactant. Lemaire[88−90] synthesized surfactant stabilized organosols by extraction of the colloidal metal into an immiscible CH_2Cl_2 phase from a preformed hydrosol. Reduction of $RhCl_3$ by hydrogen in water containing trioctylamine followed by extraction into CH_2Cl_2 gave a stable suspension of Pt. The use of trioctylamine introduced both the phase transfer agent and the stabilizer as a single reagent.

Recently Liu reported a large-scale process to produce PVP or PVA stabilized Pt and Rh nanoparticles.[91] Thus, an aqueous solution of metallic salt with polymer was lyophilized and then reduced with 40 atm of hydrogen to obtain the colloidal particles.

Finally, Finke and co-workers[8,9,23,24,92,93] used hydrogen to reduce Ir and Rh organometallic complexes. They formed zerovalent nanoparticles stabilized by a couple ammonium (Bu_4N^+)/polyoxoanion ($P_2W_{15}Nb_3O_{62}{}^{9-}$) generating electrosteric stabilization. These nanoparticles showed a great stability and their size distributions were sufficiently narrow to be qualified as monodispersions. This system is one that has a well-defined stoichiometry of formation and compositionally characterized nanoclusters.[31]

Carbon monoxide was also used as reducing agent. Kopple[94] reduced $HAuCl_4$ in the presence of polyvinyl sulfate to obtain Au colloidal particles. Carbon monoxide can also reduce PtO_2 to form Pt nanoparticles.[95]

II.2.1.1.3. Hydrides. The borohydrides ($NaBH_4$ or KBH_4) reduction of transition metal salts is the most widely used hydride reduction method of generating aqueous suspensions of metals. The stabilizing agents used in these cases are generally surfactants or water-soluble polymers. With this method Cu nanoparticles were generated by Hirai in the presence of PVP, PVE, PVA, or various polysaccharides.[96−98] Pt colloids were also stabilized by PVP with this method.[99] Mayer and co-workers have studied extensively the stabilizing polymer on the reduction of aqueous suspension of Ag, Au, Pt, or Pd by KBH_4.[64,65,67,68,100−104] They investigated cationic polyelectrolytes, polyacides, nonionic polymers, and block copolymers.

Recently, $NaBH_4$ reduction was used to obtain Au, Ag, Pt, Pd, or Cu nanoparticles stabilized by dendrimers (polyamidoamine or PAMAM).[105−114] These macromolecules allow one to obtain nearly monodispersed particles. Dimethylamineborane has been also used to prepare gold nanoparticles stabilized by hydrophobically modified PAMAM in toluene or chloroforme.[115]

Surfactants are generally used as stabilizers of aqueous colloidal suspensions of transition metal reduced by $NaBH_4$ or KBH_4. They can be cationic, anionic, or nonionic. In fact, Nakao and co-workers described the preparation of Ru, Rh, Pd, Pt, Ag, or Au nanoparticles stabilized by quaternary ammonium, sulfates, or poly(ethylene glycol).[116] Aliquat 336 (trioctylmethylammonium chloride) and CTAB or glycerol monooleate also show stabilization in water/oil microemulsions Pd[117,118] or Cu[119] nanoparticles. This reducing agent has been also used to obtain aqueous suspension of colloidal Rh stabilized by a trisulfonated surfactant.[120,121]

Several authors applied the reduction of transition metal salts to the preparation of colloidal suspensions of transition metal in organic media.

The first approach consists of reducing a metallic salt in aqueous phase by $NaBH_4$. The water is then evaporated and the solid obtained is redispersed in an organic solvent.[122] A range of methods for the phase transfer of particles has been also reported, with most studies focusing on the transfer from aqueous to organic media.[123−126]

The classical approach consists of reducing transition metal salts in an organic phase. So, Bönnemann used tetraalkylammonium hydrotriorganoborates ($NR_4(BEt_3H)$) in THF solution to reduce a wide range of Group VIB, VIIB, VIII, and IB metal halide salts (Scheme 2).[49,50,127−131] The reported particle size is generally between 1 and 10 nm, and by using appropriately substituted tetraalkylammonium salts the colloidal metal nanoparticles can be solubilized in organic media. The advantages of this system include the large-scale preparation and the wide range of metal nanoclusters available, but the main disadvantage is a lack of exact compositional characterization of the resultant colloid materials. Indeed, boron from the initial BEt_3H^- reductant is found as a 1−2% impurity in the resultant colloids.[131]

Scheme 2. Synthesis of Metal Colloid Particles Proposed by Bönneman

$$MX_n + nNR_4(BEt_3H) \xrightarrow{THF} M_{colloide} + nNR_4X + nBEt_3 + n/2H_2$$

M=group VIB, VIIB, VIII, IB metals
X=Cl, Br
R=alkyl, $C_{4\text{-}20}$

In this process, both the stabilizing agent (the NR_4^+ group) and the reducing group are coupled in the same reagent. A high local concentration of stabilizer is present during the reduction process, thus limiting the growth of the nanoparticles. Nevertheless, the reducing agents had to be generated, and this step is not straightforward. The alternative developed by Bönnemann consists of coupling the reducing agent with the transition metal salt (Scheme 3). This new compound is then reduced by hydrides (superhydride, lithium hydride...) to yield colloidal metal particles.

Scheme 3. Modified Colloid Synthesis Proposed by Bönnemann

$$(NR_4)_mMX_nY_m + nRed \xrightarrow{THF} M_{colloid} + nRedX + mNR_4Y$$

M=group VIB, VIIB, VIII, IB metals
X, Y=Cl, Br
R=alkyl, $C_{4\text{-}12}$
Red= H_2, LiH, $LiBEt_3H$, $NaBEt_3H$, $KBEt_3H$, BEt_3

With this new process, the local concentration of protecting agent is also high, and the particle sizes were reported to be between 1 and 10 nm.

Another promising approach is developed by Caruso who describes the spontaneous phase transfer of nanoparticles from organic to aqueous media. $HAuCl_4$ or Na_2PdCl_4 were reduced by $NaBH_4$ in the presence of tetraoctylammonium bromide in toluene and the rapid and complete transfer without no signs of degradation or aggregation were performed by the use of aqueous DMAP (4-(dimethylamino)pyridine) solution.[132]

II.2.1.1.4. Other Reducing Agents. Other reducing agents such as hydrazine or sodium citrate have efficiently been used in colloidal metal preparation. Hydrazine can be used in all its forms to reduce transition metals. It allows to reduce Cu[133] in the presence of PVA and PVP or Pd[118] in the cationic water-in-oil microemulsions of water/CTAB (cetyltrimethylammonium bromide), *n*-butanol/isooctane at 25 °C. Hydrazine hydrochloride[82] or sulfate[83] were tested successfully for the preparation of colloidal metals. More recently, Esumi[134,135] reduced $HAuCl_4$ by hydrazine in the presence of cationic or nonionic surfactants. The use of hydrazine as reducing agent and block copolymers as stabilizing agents was recently reported in the literature. Möller and Antonietti described the preparation of Au, Pd, Ag, or Rh nanoparticles stabilized by block copolymers such as polystyrene-*b*-polyvinylpyridine, polystyrene-*b*-poly-*m*-vinyltriphenylphosphine, or poly(ethylene oxide)-polyethyleneimine. Several polymer-stabilized systems have high thermal stability and can be used in drastic conditions.[104,136−142]

Sodium citrate was also used as reducing agent to obtain colloidal suspension of transition metals. Turkevitch and co-workers[143] studied the nucleation and growth of Au nanoparticles reduced by sodium citrate. In this case, the citrate is not only a reducing agent but also an ionic stabilizer. Citrate reduction has also been used to prepare Ir,[144] and Pt[145] nanoparticles. However, citrate anion is a noninnocent ligand and has one significant disadvantage because of the simultaneously formation of the intermediate acetone dicarboxylic acid. The unavoidable result is compositionally ill-defined colloids in opposition to focused modern nanoparticles. Fundamental studies around this research area have recently been performed by Finke and co-workers.[31]

Recently, Pal describes the synthesis of palladium particles produced in aqueous surfactant media. Their catalytic properties toward the reduction of a number of dyes in the presence of different reducing agents, such as $NaBH_4$, N_2H_4, and ascorbic acid, were studied. The dyes used were methylene blue, phenosafranin, fluorescein, 2,7-dichlorofluorescein, eosin, and rose bengal.[146,147]

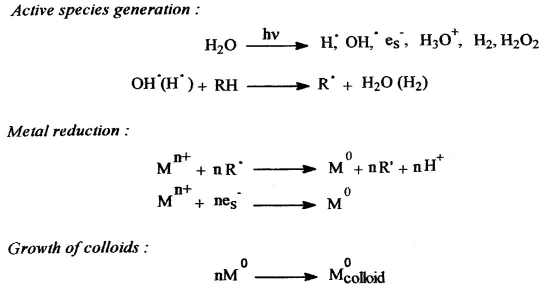
II.2.1.2. Thermal, Photochemical, or Sonochemical Decomposition. *II.2.1.2.1. Thermolysis.* Many organometallic compounds are thermally decomposed to their respective zerovalent element.

The syntheses of Pd and Pt organosols by thermolysis of precursors such as palladium acetate,[148,149] palladium acetylacetonate,[150] or platinum halides[151] have been reported in the literature. The solvents used had high boiling points such as methyl-*iso*-butylcetone. These syntheses were performed without stabilizing agents, and as a result broad size distributions and large particles were observed.

II.2.1.2.2. Photolysis or Radiolysis. Photochemical synthesis of metallic nanoparticles can be obtained either by (i) transition metal salt reduction by radiolytically produced reducing agents or (ii) degradation of an organometallic complex by radiolysis. The goal of these synthetic procedures is to obtain zerovalent metals under conditions, which prevent the formation of bulk metal. Ionization radiations are generated by X- or γ-ray generators. UV–visible irradiation is generated by Hg or Xe lamp. One advantage of radiolytic methods is that a large number of atoms is homogeneously and instantaneously produced during the irradiation thus providing favorable conditions for the formation of nearly monodispersed particles ($<15\%$ dispersion calculated by TEM imaging and NIH Image software counting of 300 particles).[13,24]

Over the past 20 years, a wide range of transition metal nanoparticles such as Ag, Au, Ir, Pt, Pd, or Cu colloids were prepared by this method.[152–162] Several reducing agents can be generated during radiolytic procedure. Thus, the radiolysis of aqueous suspension of transition metal salts produced solvated electrons or $H^{\bullet}$ and $OH^{\bullet}$ originating from water radiolysis. These species can react with the molecules in solution to give new radicals able to reduce metal salts (Scheme 4).

Scheme 4. Radiolytic Formation of Colloidal Metals



By irradiating a solution of copper perchlorate ($Cu(ClO_4)_2$) containing sodium formate Cu nanoparticles are formed through the reduction of Cu^{2+} by both solvated electrons and CO_2^- generated during radiolysis.[161] Similarly, the radiolysis of an aqueous solution of $Pd(NH_3)_4Cl_2$ and 2-propanol also results in the formation of Pd colloids by both solvated electrons and 1-hydroxy-1-ethylmethyl radicals ($(CH_3)_2COH^{\bullet}$) generated by the reaction of $H^{\bullet}$ and $OH^{\bullet}$ with 2-propanol.[162]

In an original example of radiolytic Pt colloid synthesis,[163] both the nanoparticles and the protecting polymer are produced simultaneously by radiolysis of a solution containing the monomer (acrylamide) and the metal salt (H_2PtCl_6). The radiolytic preparation of transition metal nanoparticles is also possible in organized environments such as micelles or micoemulsions.[164]

The photolysis of metal salts is also an efficient method to prepare transition metal colloids. Thus, the UV–visible irradiation of Au,[165–169] Ag,[167–170] or Pt[171] salts in reverse microemulsions in the presence of surfactants or polymers yielded metallic nanoparticles. Toshima prepared Pt[172,173] and Pd[173] colloids in the presence of micelles of a wide range of surfactants by photolysis and hydrogen reduction. They reported that the UV–visible irradiation yields smaller and better dispersed nanoparticles.

Another aspect was described by Fendler and coworkers who used UV–visible irradiation to encapsulate Pt nanoparticles into polymerized vesicles.[174] The vesicle reticulation and the colloid formation occur simultaneously during irradiation.

Mayer and Esumi reported the UV–visible photolytic synthesis of Au nanoparticles stabilized by block copolymers, polyelectrolytes,[68,102–104] or dendrimers (polyamidoamine: PAMAM).[175]

II.2.1.2.3. Ultrasonic Reduction. Sonochemistry is due to acoustic cavitation phenomena causing the formation, the growth, and the explosion of bubbles in a liquid media. The very high temperature (>5000 K), the pressure (>20 MPa), and the cooling rate ($>10^7$ K s^{-1}) reached during cavitation gave to sonicated solutions unique properties.

These extreme conditions were used by Süslick to obtain Fe particles,[176] or Co alloys[177] by reduction of metal salts. In the same way, Gedanken reported the preparation of Ni,[178] Cu,[179] Pd,[180] Fe,[181] Fe oxide,[182] or Fe nitride.[183]

The sonochemical reduction of transition metal salts occurs in three steps: the generation of the active species, the reduction of the metal, and the growth of the colloids. These three steps occur in different compartments (Scheme 5): (i) In gaseous phase into the cavitation bubbles where high temperature and pressure allow water pyrolysis to form $H^{\bullet}$ and $OH^{\bullet}$, (ii) at the interface between the cavitation bubbles and the solution, and finally (iii) in the solution.

This synthetic procedure was applied to colloidal synthesis and a wide range of surfactant or polymer stabilized transition metal nanoparticles such as Au[184] or Ag, Au, Pt, Pd[185–192] were generated. Nagata demonstrated the influence of the stabilizing agent

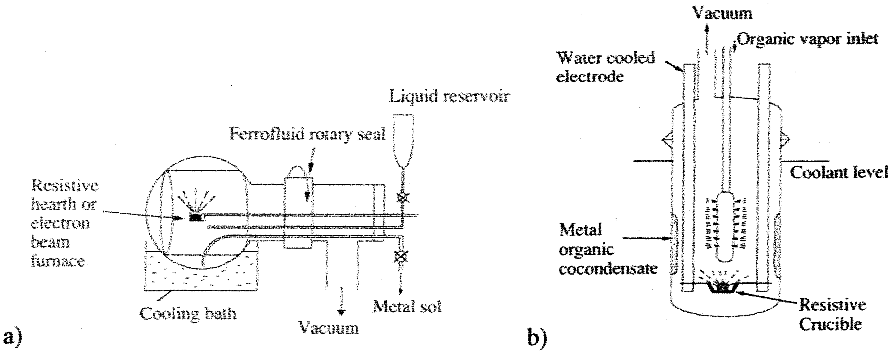
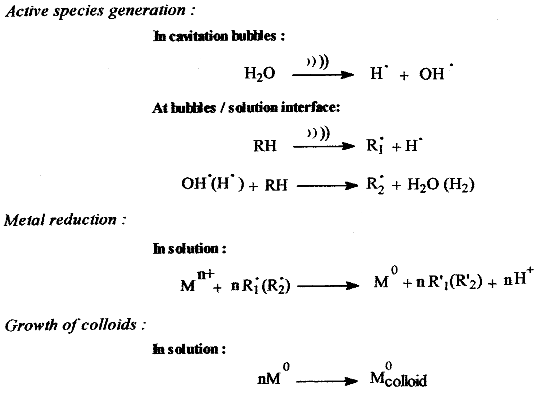


Figure 7. (a) Rotary and (b) static metal vapor reactors used in colloids preparation.

Scheme 5. Sonochemical Synthesis of Colloidal Metals



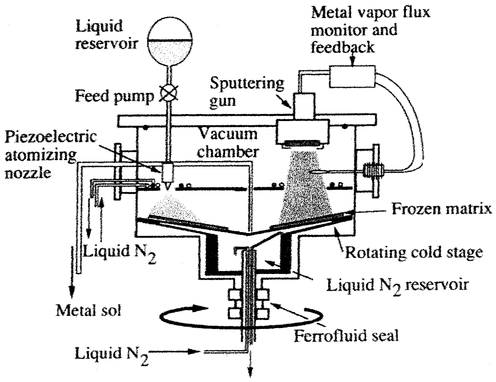


Figure 8. Schematic representation of the reactor developed by Bradley and co-workers.

and of the addition of alcohol on the kinetic of nanoparticles formation.[193,194] Finally, Gedanken and co-workers prepared quaternary ammonium stabilized Pd colloids solubilized in an organic solvent (THF).[195]

Due to the low vapor pressure of the metallic salts, the reduction cannot happen in the gaseous phase. The reduction occurs mainly at the bubble/solution interface and in solution. Nagata[194] suggested that the protecting agents in solution form alkyl radicals under sonolysis. These radicals react on transition metal salts to yield zerovalent metals (Scheme 5).

II.2.1.3. Displacement of Ligands from Organometallic Compounds. Some zerovalent organometallic complexes can be converted into colloidal suspension of metals by reduction or ligands displacements.

Using this procedure, Bradley and co-workers generated Pt and Pd (PVP) stabilized organosols. $Pt(dba)_2$[196] and $Pt_2(dba)_3$[197] dimer can be reduced by hydrogen at atmospheric pressure to obtain 2.5 nm nanoparticles. With a pressure of 3 atm, the same reduction gave 4 nm particles. The use of carbon monoxide allows also obtaining smaller particles (2 nm). With this reducing agent $Pt(dba)_2$ and $Pd(dba)_2$ can be reduced to generate nanoparticles organosols in the presence of cellulose acetate or cellulose nitrate in THF.[198,199]

The olefinic ligand reduction of zerovalent complexes can be applied to the preparation of colloidal suspensions. Thus, hydrogenation of Ru(COD)(COT) yields, in the presence of either PVP, cellulose nitrate or cellulose acetate, 1 nm Ru nanoparticles.[198,199] Spontaneous decomposition[200] or 3 atm hydrogenation[201] of $Ni(COD)_2$ has been used to prepare PVP stabilized nanoparticles soluble into CH_2Cl_2. Co, Cu, or Au PVP stabilized colloids were also generated from various organometallic complexes by this synthetic procedure.[202,203]

II.2.1.4. Synthesis by Condensation of Atomic Metal Vapor. The use of metal vapors co-condensed with organic vapors to synthesized colloidal metals in nonaqueous media is known since the dawn of the last century. However, this procedure was only extensively studied in the 70s.

This method consists of the evaporation at reduced pressure of relatively volatile metals and a subsequent co-condensation at low temperature of these metals with the vapors of organic solvents. A colloidal dispersion of the metal was then obtained by warming the frozen metal/organic mixture. The colloidal particles nucleate and grow as the frozen mixture is warmed to melting. This synthetic procedure can be conducted either in a rotating[204] or in a static[205,206] reactor (Figure 7). Generally, the metal vapors are generated from a resistively heated hearth or an electron beam furnace and condensed on the walls of the reactor together with the organic solvent vapors.

A recent reactor developed by Bradley[11] co-condenses metal vapor with aerosols of organic solvents (Figure 8). This process resolves the problems of volatile solvents.

All these systems allow the synthesis of the suspension of transition metal colloids.[207,208] Klabunde and co-workers demonstrated the preparation of various suspensions of Au and Pd by co-condensation of metal vapors in acetone. The reported particle sizes were between 5 and 30 nm.[209,210] An analogous procedure was used to condense Au in solution of polystyrene,[211] poly(methyl methacrylate),[212] or polyacetylene[212] to obtain Au colloids of 2 to 15 nm. Colloidal metals could also be generated by metal vapor condensation in fluorinated solvents.[213,214] Five nanometer Co colloids[215] stabilized by surfactants were also generated in toluene by metal vapor condensation. Smaller particles of Pd, Cu, Ni, Pt, Pr, Yb, or Er with a size about to 2 nm were obtained by co-condensation of metal vapor into solvents for the stabilization such as methylcyclohexane and *iso*-butylaluminoxane[216] or butan-2-one, methylethyl ketone (MEK), and acetone (MMK).[217−219]

The development of metal vapor routes to transition metal colloids is often limited by the apparatus. The advantage of this metal atom method is to generate zerovalent nanoparticles stable for several months, but the main disadvantage is the control of the size. This parameter is essential for reproducible catalytic applications and can require sophisticated metal vapor reactor for the control of the preparative conditions such as inert gas and gas pressure.

II.2.1.5. Reduction by Electrochemical Methods. M. T. Reetz at the Max Plank Institut has developed an electrochemical method for the preparation of transition metal nanoparticles.[220,221] This large-scale synthetic procedure allows one to obtain size-controlled particles.

A sacrificial anode is used as a metal source. This anode is oxidized in the presence of quaternary ammonium salt, which is both the electrolyte and the stabilizing agent. The ions are then reduced at the cathode to yield the metallic nanoparticles. With this process, Reetz and co-workers were able to generate acetonitrile/THF dispersed Pd colloids[221] with various sizes. The mechanism proposed by the authors consists of (i) dissolution of the anode to form metal ions (oxidation of Pd to Pd^{2+}); (ii) migration of the metal ions to the cathode; (iii) reduction of the metal ions at the surface of the cathode; (iv) aggregation of the particles stabilized by the ammonium ions around the metal cores; and then (v) precipitation of the Pd nanoparticles (Figure 9).

This process presents several advantages: (i) particle size can be controlled by varying the current intensity[221] (higher current intensity gives smaller particles); (ii) isolation of the nanoparticles is simple as they precipitate out of the solvent when formed; and finally (iii) the synthesis occurs with good yields (>95%).

This synthetic procedure can be applied to easily oxidized transition metals such as Ni or Cu. The solubility of the colloids obtained can be modulated from nonpolar solvents such as pentane to polar solvents as water by changing the polarity of the protecting agent (tetraalkylammonium halide for apolar solvents or sulfobetaine for polar solvents).[222]

For less easily oxidized metals such as Pt, Rh, or Ru, the anode and cathode used are made of Pt and the metallic precursor is a transition metal salt.[222] In this new process the anode is no more sacrificed and the metallic precursor is reduced by electrolysis in the presence of a quaternary ammonium salt which is both the electrolyte and the stabilizing agent.

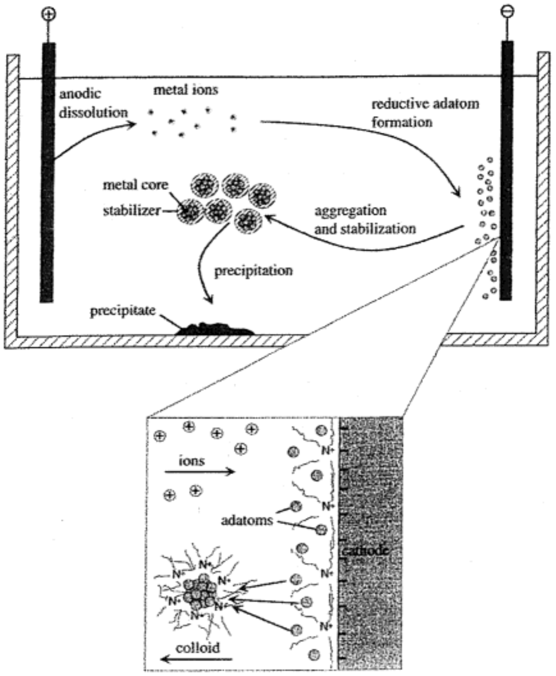


Figure 9. Reetz and co-workers' proposed mechanism for the formation of electrochemical synthesized metal colloids.

II.2.2. Preparation of Immobilized Nanoparticles on Solid Support

The application of liquid suspensions of metal nanoparticles in catalysis is limited by several drawbacks. In fact, with these systems the separation of the products and the recycling of the catalyst are not straightforward. The immobilization of such materials on a solid support seems to be an interesting alternative since the catalyst can be recycled by simple filtration. However, supported nanoparticles are generally less satisfactory because salts and other stabilizers also adsorbed to the surface often kill catalytic activity.[223] Several immobilization methods and several supports have been investigated in the literature for the immobilization of metal colloids. Transition metal nanoparticles can be either adsorbed on inorganic support or chemically bonded to polymeric support.

II.2.2.1. Nanoparticles Adsorption on Support. The most widely reported supports used to adsorb colloidal nanoparticles are inorganic solids such as charcoal, silica, alumina or oxides such as TiO_2 or MgO. Adsorption generally occurs as follows: (i) preparation by reduction of a liquid suspension of the stabilized colloidal metal, (ii) nanoparticles impregnation on the support, and finally (iii) washing of the solid obtained. The main advantage of this process is that the size of the colloidal nanoparticles is generally independent from the support, which is not the case for heterogeneous catalysis where the reduction occurs after the impregnation of the metallic precursor.

Bönnemann prepared with their method a wide range of quaternary ammonium salts stabilized metal nanoparticles in THF. They immobilized these particles by simple impregnation by stirring a nanoparticle suspension on charcoal.[47−50,127,130,131]

With the same procedure, Reetz deposited on charcoal or silica electrochemically synthesized nanoparticles.[221,222,224] The support is added either during the preparation of the nanoparticles or after the formation of the nanoparticles. Reetz also immobilized Pd colloids on alumina disk.[225] They demonstrated various adsorption behavior depending on the stabilizing agent used. With sulfobetaine the Pd nanoparticles were mainly on the surface of alumina disks whereas they adsorb up to the core of alumina disks when tetraalkylammonium bromide stabilizers were used. In all cases, the nonalteration of structure and particle size were checked by transmission electron microscopy.

Liu reported the immobilization of Pd, Pt, or Rh colloids stabilized by PVP or PVA on silica.[226,227] The authors explained the immobilization of the metal nanoparticles by adsorption of the protective polymers/metal complex on silica. The authors suggested that this adsorption was due to hydrogen bonds formed between polymers and hydroxyl functions of silica.

Several recent studies present new procedure for the generation of Au[228] or Pd[229] nanoparticles respectively dispersed within pores of mesoporous silica or in the interlamellar space of silicates such as montmorillonite, saponite, or kaolinite. Dékány and Király reported the preparation of Pd nanoparticles via reduction by ethanol of Pd acetate in the adsorption layer. Characterization of these materials (TEM measurements, X-ray diffraction, N_2 gas sorption...) were performed.[229−232]

On the fringe of these immobilization procedures on inorganic supports, some examples of direct synthesis of Pt or Pd nanoparticles on polymeric support such as latex microspheres have been reported.[233−235] The nanoparticles adsorption and stabilization at the surface is dependent on the polarity of the latex used. In the same way, Toshima and co-workers[236−238] generated Pd colloids supported on chelating resins by reduction of $PdCl_2$ in the presence of resin. Nakao[239] realized the adsorption of aqueous suspensions of Rh, Pd, Pt, Ag, or Au colloids stabilized by a wide range of surfactants on ion-exchange resins. There is actually a large number of heterogeneous catalysts prepared by direct synthesis of metal nanoparticles on polymeric supports which have been reported in the literature. Several preparations and catalytic applications of dispersed metal catalysts supported on organic functional polymers have been recently described by Králik and Biffis.[240]

II.2.2.2. Colloids Grafting on Support. Another way to immobilize metallic nanoparticles is to graft colloids on solid support. A wide range of chemical bonds have been tested to immobilize nanoparticles on supports.

Hiraï[241,242] and Toshima[237,243] grafted Pt and Rh colloids onto polyacrylamide gel having aminoethyl groups. The immobilization is generated by formation of amide bonds by reaction of ester functions of the protecting polymer copolymer PVP/methyl polyacrylate copolymer) with amine functions of the gel (Figure 10). According to transmission electron microscopy, the grafted nanoparticles remain unchanged during the immobilization process. No metal leaching was observed by the author during the dispersion of the support in liquid phase.

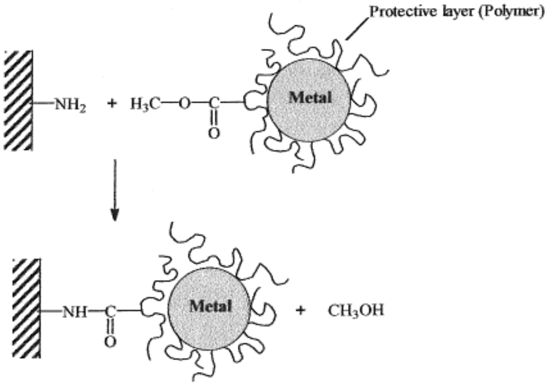


Figure 10. Covalent immobilization of metal colloid particles.

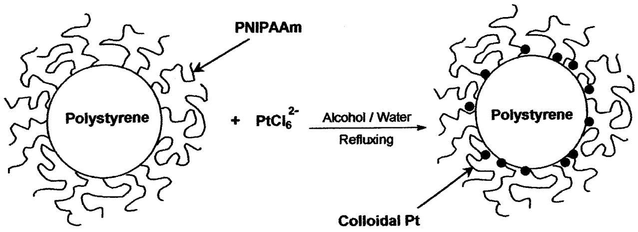


Figure 11. Pt colloids supported on polystyrene microspheres.

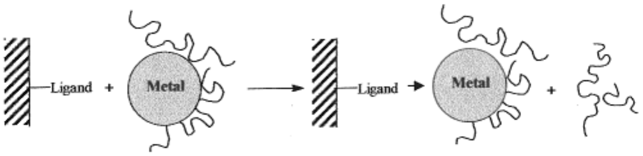


Figure 12. Coordinated immobilization of metal colloid particles.

Akashi prepared transition metal nanoparticles covalently bonded to the support through protecting polymer.[244−246] The supports used were polystyrene microspheres with surface-grafted PNIPAAm.[245,246] The synthetic procedure consists of the reduction of H_2PtCl_6 in the presence of the microspheres. Thus, the PNIPAAm chains will stabilize and maintain dispersed the Pt nanoparticles onto the surface of the microspheres (Figure 11).

Liu developed an immobilization procedure based on the coordination of a metal by a thiol-modified silica (Figure 12).[247,248]

Nevertheless, the main drawback of the whole procedure is that it requires a complex modification step of the support. Moreover, the sulfur compounds used in this method are able to poison the catalyst. Consequently, Liu modified their system by using triphenylphosphine as ligand.[249]

II.3. Bimetallic Colloids Preparation

The preparation and catalytic use of bimetallic colloids[250] appeared in the literature. Bimetallic colloids are constituted of two distinct metals. Such compounds often showed better activity and selectiv-

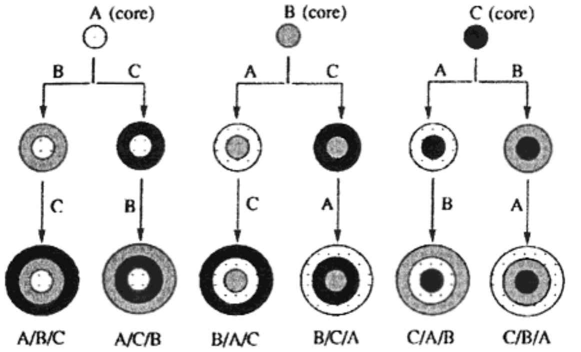


Figure 13. Illustration of the living metal–polymer approach to the synthesis of multimetallic nanoclusters.

ity compared to monometallic colloids. These new properties can be due to a synergy between the two metals forming particles,

The preparation of these bimetallic materials can be conducted either by simultaneous or successive reduction of two metallic precursors. The coreduction is the most widely reported method since this procedure is easy to implement. Most of the synthetic procedures used to prepare monometallic particles can be applied to bimetallic particles synthesis. An "idealized" illustration of the living metal–polymer approach to the synthesis of multimetallic nanoclusters or "nano-onions" has been reported by Finke and co-workers (Figure 13). This approach based on an autocatalytic surface growth mechanism must give at least in principle a well-defined initial structure and a layer thickness. Several conditions are listed to consider geometric isomers of bi-, tri-, and higher multimetallic nanoclusters formation.[7–10]

II.3.1. Coreduction of Metallic Precursors

The principles of this synthetic procedure are the same as those applied for monometallic nanoparticles. The metallic precursors are reduced in the presence of stabilizing agents to prevent aggregation of the formed particles. So the wide range of synthetic procedures used for the monometallic particle synthesis was tested for the preparation of bimetallic colloids.

Polymer stabilized bimetallic nanoparticles in hydro alcoholic media were prepared by simultaneous reduction of two transition metal salts in refluxing alcohol. For example, PVP stabilized colloidal suspension of Pd/Pt bimetallic particles was generated by refluxing an aqueous/alcohol mixture containing $PdCl_2$ and H_2PtCl_6.[251–255] Following the same procedure, colloidal suspensions of Au/Pd,[256] Pt/Rh,[257] Pt/Ru,[258] Pd/Ru,[259] or Ag/Pd[260] stabilized by PVP were generated by coreduction in refluxing alcohol of the corresponding transition metal salts. Other polymer protecting agents such as PNIPAAm[261] were also used.

Easily oxidized metal colloids such as Cu or Ni are difficult to prepare in comparison with transition metal nanoparticles made of Rh, Pt, or Ru. Nevertheless, Cu/Pd,[262–264] Cu/Pt,[262] or Pd/Ni[265,266] bimetallic particles stabilized by PVP were obtained by coreduction of the corresponding metallic hydroxides in refluxing glycol.

Thermal decomposition of metallic acetates has also been used to prepare bimetallic colloids. Bradley[267] reported the synthesis of PVP stabilized Pd/Cu bimetallic nanoparticles by thermal decomposition of palladium acetate and copper acetate in a high boiling point solvent (ethoxyethan-2-ol).

Gamma irradiation has also been applied for the preparation of bimetallic particles. Delcourt and coworkers generated Ag/Pt[268] colloids by irradiation of a solution containing Ag_2SO_4 and K_2PtCl_4. These nanoparticles were stabilized either by PVA or by polyacrilic acid (PAA). Henglein reported also the use of this method to prepare various polymer stabilized transition metal bimetallic nanoparticles.[269] Au/Pt nanoparticles stabilized by nonionic surfactants have also been synthesized by γ irradiation of a mixture of $NaAuCl_4$ and $NaPtCl_6$.[270]

The preparation of bimetalic nanoparticles in water-in-oil microemulsions has been also described. Au/Pt, Pt/Pd, and Cu/Au systems were essentially reported.[271–273]

The use of tetraalkylammonium hydrotriorganoborates ($NR_4(BEt_3H)$) as reducing agent is reported by Bönnemann for the preparation of a wide range of bimetallic colloidal particle.[127,128,274–276]

Organometallic complexes have also been used as precursors of bimetallic colloids. Chaudret reduced with hydrogen, $Pt(dba)_2$, and Ru(COD)(COT) in various proportions, to obtain PVP stabilized Pt/Ru nanoparticles.[277] An original procedure developed by Esumi[278] was the synthesis of Ag/Pd or Ag/Pt nanoparticles by photo or $NaBH_4$ reduction of silverbis(oxalato)palladate or silverbis(oxalato)platinate complexes.

The electrochemical synthesis of metal colloids developed by Reetz allows also the preparation of bimetallic nanoparticles. To do so, two different sacrificial metallic anodes and a Pt cathode were immersed in an electrolyte in the presence of a stabilizing agent (tetraalkylammonium salt).[280] The metallic ions were generated by current and reduced at the cathode to give tetraalkylammonium stabilized bimetallic colloids.

II.3.2. Successive Reductions of Metallic Precursors

A successive reduction of transition metal salts is the most suitable method to synthesize core/shell bimetallic colloids. The deposition of a second metal on a preformed metallic particle seems to be a good procedure as well. The second metal has to be deposited on the whole surface of the preformed monometallic nanoparticles.

A preliminary synthesis achieved by Toshima to generate core/shell Au/Pd[281] nanoparticles conducted in fact to randomly distributed Au/Pd bimetallic nanoparticles. On the other hand, the preparation Au/Pd and Au/Pt bimetallic nanoparticles stabilized by such water-soluble ligands as $P(m\text{-}C_6H_4SO_3Na)_3$ or $p\text{-}H_2NC_6H_4SO_3Na$ has been described by Schmid.[282,283]

Henglein has prepared bimetallic gold and platinum particles of the Pt/Au, Au/Pt core–shell type and bimetallic $Pd_{core}Au_{shell}$ using hydrogen reduction and radiolysis techniques. Finally, Radiolytic methods are applied to synthesize trimetallic $Pd_{core}Au_{shell}Ag_{shell}$ particles in aqueous solution, using sodium citrate as stabilizer. Optical spectra of this structure are reported.[284−286]

Toshima developed an original synthetic procedure for the preparation of core/shell bimetallic colloids. They generated PVP stabilized Pd/Pt bimetallic colloids with a Pd core.[287] The principle of this method is that hydrogen can easily be adsorbed on Pd surface to form a metal−H bond. This H atom is a good reducing agent, and the Pt ions added to a preformed Pd colloidal suspension are easily reduced by the adsorbed hydrogen atoms. The zerovalent Pt formed will deposit onto the Pd surface to generate a perfect core/shell structure.

Recently, Pal prepared bimetallic Au/Ag particles with a core−shell type structure by a UV-photoactivation technique.[288]

II.4. Conclusion

Stable transition metal colloidal suspensions can be obtained by a wide range of procedures. This synthetic diversity allows one to choose the most suitable method for a specific application. Recent kinetic and mechanistic studies will probably generate an increasing development of various compositionally characterized nanoclusters in the field of colloidal chemistry.[8] In the future, the synthesis of near-monodispersed nanoparticles with their known size, size-distribution, composition, and shape will be more relevant than traditional colloids poorly defined.

In the past few years, chemists and physicochemists have been more and more interested in structural studies of catalysts with a view to increasing their efficiency. Today, many technics are available to establish particle size and overall composition. Sophisticated characterization techniques include atomic force microscopy (AFM), scanning tunneling microscopy (STM), high-resolution electron microscopy (HREM), energy-dispersive X-ray spectroscopy (EDX), extended X-ray fine structure (EXAFS), X-ray photoelectron spectroscopy (XPS) but also traditional methods such as UV−Visible spectroscopy, NMR, infrared spectroscopy, and Raman spectroscopy (surface enhanced RS).[13,289] Microscopy is a valuable observation technique for preliminary characterizations of nanoparticles. Recently, nanoparticles have been observed by AFM or by STM.[290−293] In addition to that, the size and distribution can be determined by HREM.[39−41,51,294,295] The composition can be elucidated with the help of EDX[267,276,278,279,282,283,296,297] and XPS[51,245,246,262,297] allow one to know the oxidation state of the metal. Finally, the structure of these small particles can be investigated with EXAFS.[46,252,253,257,266,298,299]

Although numerous useful information are more or less readily available concerning their metallic core the problem related to a more precise knowledge of the environment between metal atoms and colloidal particles remains difficult to solve.

In few cases, protective agents around the surface of transition metal particles have been characterized. Therefore, Creighton and co-workers have observed the pyridine adsorption on Au or Ag by Raman spectroscopy.[300,301] Wiesner[302] has studied by SERS[302,303] the stabilization of Ag colloids by cetyltrimethylammonium bromide (CTAB) in aqueous phase. Classical techniques such as microscopic or ^{13}C NMR analysis or electrochemical studies can also be used to obtain information on the surroundings of the particles.[304−309]

III. Catalytic Applications of Metal Colloids

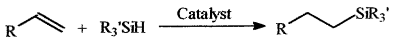
The catalytic properties of transition metal colloids have generated great interest over the past decade.[7,13,15,16] In fact, these new catalysts often combine the precious characteristics of higher reactivity and selectivity. This can be explained by the structural specificities of the colloidal state of the catalyst: these materials have a very large specific surface, and consequently a large percentage of catalyst’s metal atoms is available to the substrates. Several studies in metal particle catalysis research area have been performed to know the true number of catalytically active surface sites.[297,310−313] The true turnover frequency (moles of product/(moles of active metal atoms × time)) is almost never, but needs to be calculated to evaluate the true rate per catalytically active metal atom. The poisoning methods on nanoparticles should be, therefore, a more generally needed experiment.

Thanks to their properties, it is obvious that these materials have been tested as catalyst for various kinds of reactions. Transition metal colloids are widely used as catalyst for hydrogenation of olefins. More recently, the range of reactions investigated has increased. Four classes of reactions will be considered in this paper: (i) hydrosilylation, (ii) oxidation, (iii) C−C coupling reactions, and (iv) selective hydrogenation.

III.1. Hydrosilylation Reactions

The hydrosilylation reaction (Scheme 6) is one of the most important ways to prepare silicone polymers.

Scheme 6. Catalytic Hydrosilylation Reaction



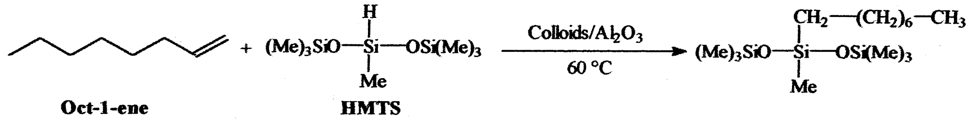
Organometallic complexes with Co, Ni, Pd, or Pt were used in homogeneous phase to catalyze this reaction. However, these complexes are only precursors to the really active species: a colloidal suspension of metal particles generated during an induction period.[314−318]

With transmission electron microscopic observation, Lewis[314,316−318] demonstrated the presence of Pt nanoparticles. These particles were generated by the reduction of organometallic complexes by silanes used as reagents.

With these works in mind, Schmid[223] used Pt colloids and Pt/Au or Pt/Pd bimetallic colloids supported on alumina to catalyze the hydrosilylation of oct-1-ene with heptamethyltrisiloxane (HMTS) (Scheme 7).

The final product was obtained with a good selectivity after 24 h. When the Pt/Pd colloids were used, the catalytic activity increased to raise 96% of

Scheme 7. Hydrosilylation of Oct-1-ene with Colloid Metal Particles

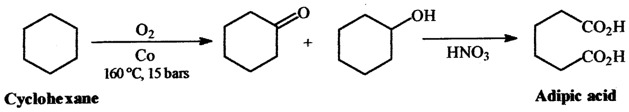


conversion in 12 h. These colloids were recovered without major loss of activity by filtration of the support.

III.2. Oxidation Catalyzed by Metallic Nanoparticles

Most reactions catalyzed by metal colloids concern reduction reactions. Only a few examples of oxidation reactions were described in the literature. However, these reactions represent important industrial catalytic processes which may benefit of progresses in the field of nanoclusters catalysis. For example, the synthesis of adipic acid, which is an essential intermediate for the preparation of Nylon 6 and Nylon 6,6, is industrially obtained by catalytic oxidation of cyclohexan with Co complexes (Scheme 8).

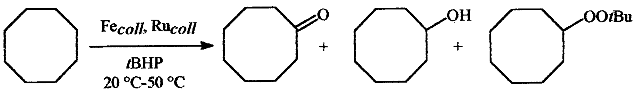
Scheme 8. Catalytic Oxidation of Cyclohexane with Co and O_2



III.2.1. Hydrocarbon Oxidation

The oxidation of cycloalkane by tBHP catalyzed by transition metal colloids has been studied (Scheme 9).[319,320]

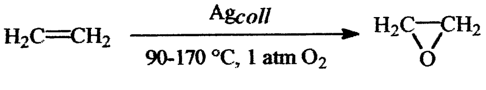
Scheme 9. Catalytic Oxidation of Cyclooctane with *t*BHP and Colloidal Metals



This reaction was performed under different conditions: with Fe nanoparticles in reverse microemulsions or with Ru colloids in biphasic water/organic media. The substrate cyclooctane was used as the organic phase, whereas the Ru nanoparticles were dispersed in the aqueous phase. This biphasic system allows the recycling of the aqueous phase containing the Ru particles without any loss of activity. After optimizing the reaction conditions, cyclooctanol and cyclooctanone were the main reaction products.

Toshima[321,322] used Au colloids stabilized by PVP or by sodium polyacrylate to oxidize ethene (Scheme 10).

Scheme 10. Catalytic Oxydation of Ethene



The reaction catalyzed by colloids stabilized by sodium polyacrylate at 170 °C and under oxygen/ethene atmosphere gave the best results. In fact, these nanoparticles have a higher thermal stability. The addition of Cs(I) or Ru(VII) ions permits one to increase the catalytic activity.

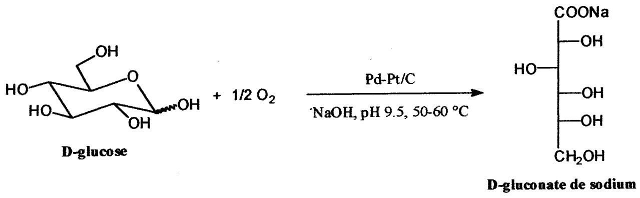
III.2.2. Oxidation of p-Phenylenediamine Derivatives

Spiro and co-workers have described that the oxidation by $Co(NH_3)_5Cl^{2+}$ of *p*-phenylene diamine derivatives such as *N*,*N*,*N'*,*N'*-tetramethyl (TMPPD) or *N*,*N*-diméthyl (DMPPD) in an aqueous water/AOT/*n*-heptane microemulsion is catalyzed by nanoparticles of palladium.[323,324] The kinetic and mechanistic formations of *p*-semiquinonediimine derivatives have been described. The initial rates of the catalyzed reaction at 25 °C were found to be first order in palladium, and the authors conclude that the rate-determining step of the catalysis is probably diffusion of $Co(NH_3)_5Cl^{2+}$ ions through a layer of adsorbed DMPPD to reach the metal. Finally, electrons are transferred via the metal from the adsorbed DMPPD molecules to $Co(NH_3)_5Cl^{2+}$ ions. Pd nanoparticles of 2.5 nm have been characterized by HRTEM and SAXS size measurements.

III.2.3. Glucose Oxidation

At the present time, oxidation of D-glucose to obtain D-sodium gluconate is performed by enzymatic oxidation. Recently, a bimetallic Pd/Pt catalyst supported on charcoal was developed by Degussa to perform this reaction under oxygen atmosphere and in a basic media (Scheme 11).

Scheme 11. Oxidation of D-Glucose



Bönnemann conducted this reaction with bimetallic Pt/Pd colloids stabilized by tetraalkylammonium salts. These nanoparticles were obtained by coreduction of Pt and Pd salts and then immobilized on charcoal.[325,326] The activity and lifetime of this new catalyst was investigated and showed a better activity than the Degussas's catalyst. Authors propose that the quaternary ammonium salt present at the surface of the bimetallic particles protects them from poisoning. This stabilization of transition metal nanoclusters is the subject of a confusing literature. The confusion on the direct interaction of R_4N^+ with the metal surfaces can be traced to 1988 and 1995 papers showing a direct coordination of the ammonium salt to the Ag(0) or Pd(0) surfaces, respectively.[302,304] Moreover, elemental analyses often show the presence of chloride, bromide, or other anions;[130,131] hence, there is no compelling evidence for a chemically implausible direct adsorption of the

R_4N^+ to an electrophilic metal surface as written but rather that the anions are adsorbed. A SERS study of $(CH_3)_4N^+$ adsorbed on silver electrodes demonstrates that halide anions indeed exist between the adsorbed R_4N^+ cations and Ag^+ cations on the electrode surface.[327] Unambiguous studies on anion stabilization of nanoclusters have recently been reported by Finke and co-workers.[31]

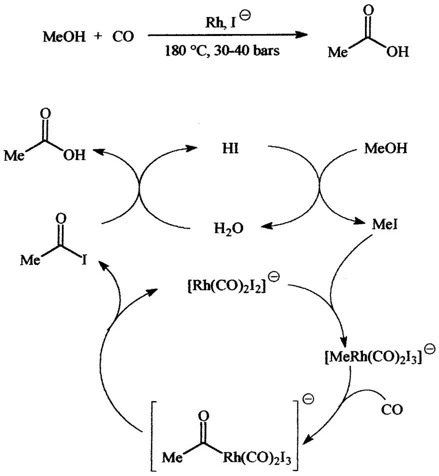
III.3. C−C Coupling Reaction Catalyzed by Metallic Nanoparticles

The most important industrial application of homogeneous phase catalyzed reaction is the hydroformylation of olefins. This transformation is not the only industrially used C−C coupling reaction. In fact, the synthesis of vitamin E developed by Rhône-Poulenc involved a coupling step between myrcen and methyl acetylacetonate. Rh molecular complexes catalyze these coupling reactions.[328] Other kinds of C−C coupling reactions such as Heck or Suzuki couplings using Pd complexes have also proved useful for the tool-boxes of organic chemists.

III.3.1. Carbonylation of Methanol

The carbonylation of methanol is one of the most important industrial processes. The process used was developed by Monsanto. It replaces the Wacker process and uses a homogeneous Rh catalyst (Scheme 12).[329]

Scheme 12. Monsanto Process for Carbonylation of Methanol

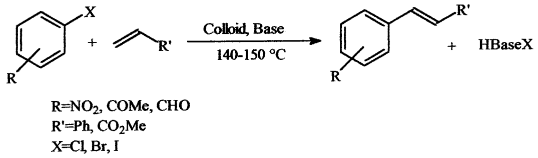


Liu[330] have tested Rh nanoparticles stabilized by PVP as catalyst for this reaction. The colloidal suspensions were stable under the drastic reaction conditions required (140 °C, 54 bar) but were less active than the Rh complex used in the Monsanto process. Spectroscopic investigations conducted during the reaction (IR, CO adsorption and XPS) have demonstrated the presence of Rh(I) species. As expected, the active species were not the Rh nanoparticles but the Rh(I) species generated by oxidation of Rh(0) nanoparticles by methyl iodide.

III.3.2. Heck Reactions

During the past decade, several groups have tried to use colloidal suspensions to catalyze Heck coupling reaction (Scheme 13).

Scheme 13. Colloidal Metal as Catalyst for the Heck Coupling Reaction



Herrmann was the first to describe the use of Pd nanoparticles to catalyze this coupling reaction.[331] The Pd colloids were prepared by the Bönnemann's method and were stabilized by a quaternary ammonium salts: the tetraoctylammonium bromide.

Reetz has also used Pd to prepare via their electrochemical process a colloidal suspension in propylene carbonate.[332] These nanoclusters were efficient to catalyze Heck coupling reactions at high temperature (160 °C).

And finally, Antonietti,[141] Bradley,[142] Crooks[333] have respectively considered block copolymers (polystyrene-*b*-poly-4-vinylpyridine), poly(vinylpyrrolidone), or perfluorinated polyether-poly(propylene imine) (PPPI) dendrimers to stabilize Pd nanoparticles used in Heck coupling reactions.

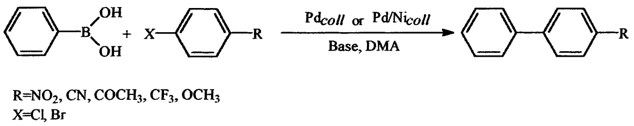
In all cases, the catalytic activity observed during the Heck coupling depended on the substrate studied. Generally, a higher activity was observed when arenes are substituted with an electron-withdrawing group such as nitro or carbonyl. These observations are similar to those observed in the case of Pd molecular complexes. More investigations are required to determine the true catalyst and to characterize it.

Among these different suspensions, the colloids developed by Antonietti and Bradley seem to be the most interesting. In fact, these particles stabilized by a block copolymer have a higher thermal stability (at least 140 °C) and catalytic lifetime.

III.3.3. Suzuki Reactions

Reetz and co-workers have described the use of Pd or Pd/Ni nanoparticles as catalysts for the Suzuki coupling reaction (Scheme 14).[334]

Scheme 14. Colloidal Metal as Catalyst for the Suzuki Coupling Reaction



The colloidal suspensions stabilized by tetrabutylammonium bromide, used as catalyst for the Suzuki reaction, were prepared by their electrochemical method and were redispersed in DMA. As for the classical Suzuki reaction, bromide derivatives showed a better activity than chloride derivatives. Moreover, the use of substrates with electron-withdrawing substituents increases the activity. Finally, bimetallic Pd/Ni colloids lead to a better conversion rate.

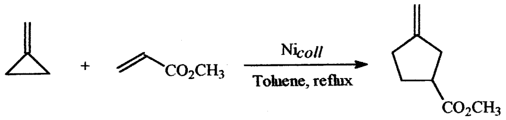
Recently, El-Sayed describes the synthesis of palladium nanoparticles prepared in the presence of different stabilizers such as poly(amido-amine) dendrimers (PAMAM), block copolymer polystyrene-*b*-

poly(sodium acrylate), poly(*N*-vinyl-2-pyrrolidone) and PVP. The effects of these stabilizers on the metallic nanoparticles stability and catalytic activity in the Suzuki reactions in aqueous solution have been investigated.[335,336]

III.3.4. Other C–C Coupling

In 1998, Reetz has prepared electrochemically Ni colloids stabilized by tetradodecylammonium bromide. These nanoparticles were used for the [3+2] cycloaddition of methylene cyclopropane on methyl acrylate (Scheme 15).[337]

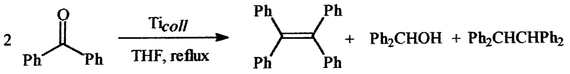
Scheme 15. [3+2] Cycloaddition Reaction Catalyzed by Nickel Colloids



The Ni nanoparticles were dispersed in THF or immobilized on alumina. However, only supported particles lead to a significant activity. Furthermore, the activity is poor compared to the classical catalyst used for this reaction: $Ni(COD)_2$.

The McMurry coupling reaction of benzophenone to form tetraphenylethylene was also investigated with Ti colloids (Scheme 16).[338]

Scheme 16. McMurry Reaction Catalyzed by Ti Colloids



This reaction occurs with the formation of 15% side products. Similar activity and selectivity were obtained for the coupling reaction of acetophenone into (*Z*)-2,3-diphenylbut-2-ene or for the coupling of benzaldehyde into (*E*)-stilbene.

Recently, Kobayashi has developed a Lewis acid-surfactant-combined catalyst (LASC) for various typical carbon–carbon bond-forming reactions such as aldol, allylation, and Mannich-type reactions in water. LASCs are composed of water-stable Lewis acidic cations such as Scandium and anionic surfactants.[339] The characterization of the colloidal particles has been carried out by means of dynamic light scattering, light microscopy, transmission electron microscopy, and atomic force microscopy.

III.4. Hydrogenation Catalyzed by Metal Nanoparticles

The use of dispersed or immobilized transition metal nanoparticles as catalysts for hydrogenation reactions of terminal, internal, or cyclic olefins has been widely studied.[55,68,107–109] In fact, transition metal colloids have recently shown good activities in chemo-, regio-, stereo-, or enantioselective hydrogenations of various substrates.

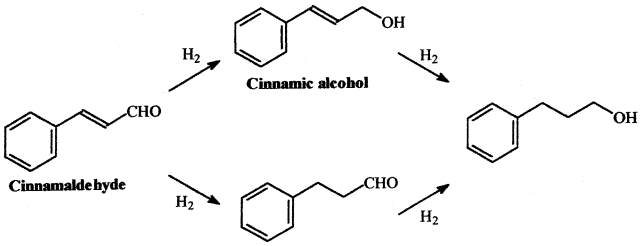
III.4.1. Chemoselective Hydrogenations

Transition metal nanoparticles were tested for chemoselective hydrogenation of unsaturated carbonyls into unsaturated alcohols or for hydrogenation of chloronitroaromatics into chloroanilines.

III.4.1.1. Selective Hydrogenation of Unsaturated Aldehydes. Selective hydrogenation of unsaturated aldehydes to form unsaturated alcohols is a crucial step for the preparation of several compounds used in fine chemistry and particularly for fragrances. Nevertheless, the reduction of carbonyl group in the presence of a double bound is not straightforward since most of the conventional catalysts reduce preferentially the double bond to give the saturated aldehyde.

Recently, Liu and co-workers achieved the reduction of cinnamaldehyde into cinnamic alcohol with Pt nanoparticles stabilized by PVP as catalyst (Scheme 17).[340–346]

Scheme 17. Possible Pathways for the Hydrogenation of Cinnamaldehyde



The reaction was performed under 40 atm of hydrogen and a selectivity of 12% in cinnamic alcohol was obtained after 38% conversion. Selectivity of 98.5% or 98.8% in cinnamic alcohol for 83% of conversion could be reached by addition of various cations such as Fe^{3+} or Co^{2+}.[340,341] The authors proposed that an interaction between the cation and the oxygen of the carbonyl could facilitate the adsorption of the double bound on the metallic surface, thus justifying the activity and selectivity obtained with their Pt colloids (Figure 14).

Liu used Pt/Co bimetallic colloids stabilized by PVP to perform this reaction with a cinnamic alcohol selectivity of almost 100% for 93% of cinnamaldehyde transformed.[343,344] Similar results were obtained using Pt colloids immobilized onto various supports such as polystyrene, alumina, Ti(IV) oxide, or Mg(II) oxide.[345,346]

Ru or Pt nanoparticles stabilized by PVP were employed as catalyst to achieve the hydrogenation of citronellal into citronellol (Scheme 18) with a selectivity of 95%.[249,347,348]

III.4.1.2. Selective Reduction of Chloronitrobenzene. Halogenated aromatic amines are important intermediates of the herbicide and pesticide chemistry. The classical approach to synthesize these

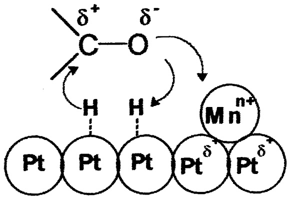
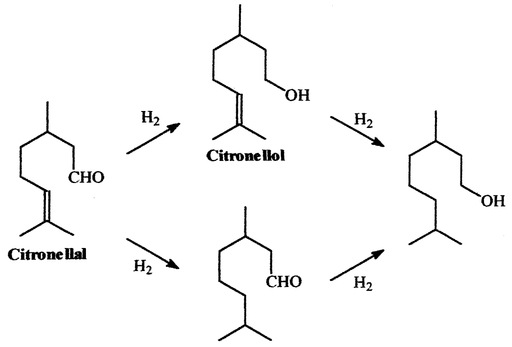


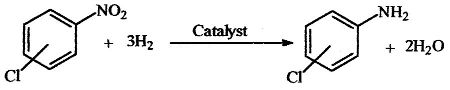
Figure 14. Mechanism proposed by Liu and co-workers to explain the influence of cations on selectivity.

Scheme 18. Possible Pathways for the Hydrogenation of Citronellal



compounds is based on the use of hydrochloric acid. An alternative reaction is to perform the selective hydrogenation of chloronitrobenzene with heterogeneous catalysts (Scheme 19). In such a process, it is necessary to reduce the nitro group without dehalogenation.

Scheme 19. Hydrogenation of Chloronitrobenzene



Several research groups tried to carry out this reaction with the help of transition metal colloids. Liu studied the atmospheric pressure hydrogenation of *o*-chloronitrobenzene into *o*-chloroaniline catalyzed by various colloidal suspensions such as Pt[349,350] and Ru[351] nanoparticles or Ru/Pt[352] Ru/Pd[352] or Pd/Pt[255] bimetallic colloids. The best results in terms of selectivity and activity were obtained with the Ru and the Ru/Pt colloids, which showed a good stability. Here again, the authors observed that addition of metallic ions (Co^{2+}) during the reaction increased the catalytic activity. All these reactions were conducted with supported colloids.[249,346]

The same procedure was used by Liao to obtain *p*-chloroaniline by hydrogenation of *p*-chloronitrobenzene. The catalysts were bimetallic suspensions of Pd/Ru or Pd/Pt stabilized by PVP.[259,353]

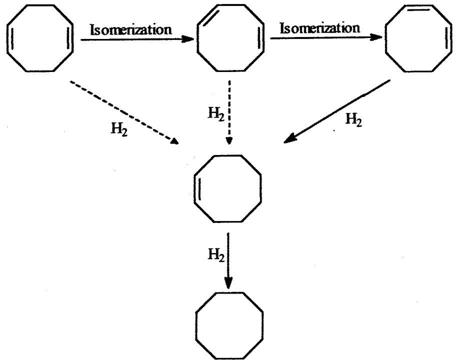
Bönnemann and co-workers were able to hydrogenate 3,4-dichlorobenzene with Pt nanoparticles immobilized on charcoal and stabilized by several betains.[311] These catalysts showed a good activity and stability under the drastic reaction conditions (150 °C, 100 atm of hydrogen). Recently, Pal reported for the first time the catalytic reduction of several aromatic nitro compounds to the corresponding amino derivatives using $NaBH_4$ by coinage of metal nanoparticles (Cu/Ag/Au).[354] The catalytic efficiency of these colloids for electron transfer is explained by their size-dependent redox properties.

III.4.2. Regioselective Hydrogenations

Various regioselective hydrogenation reactions can be catalyzed by transition metal colloids. For example, hydrogenation of diene into monoene or hydrogenation of acetylenic compounds bearing a double bound into diene were catalyzed by transition metal colloids.

III.4.2.1. Hydrogenation of Conjugated Dienes into Monoolefins. Hirai studied extensively the use of colloidal catalysts for the selective hydrogenation of dienes to form monoenes. Hydrogenation of cyclopentadiene into cyclopentene was performed with a colloidal suspension of Pd particles stabilized by PVP.[355,356] Cyclooctene was also obtained by selective hydrogenation of cycloocta-1,5-diene with Pd colloids.[357] Hydrogenation of the 1,3-isomer occurs faster than hydrogenation of 1,5- and 1,4-isomers. In fact, these two compounds isomerize first to form conjugated dienes and which are partially hydrogenated (Scheme 20). The selectivity of the olefin increases with the diminution of the size of the Pd nanoparticles.

Scheme 20. Hydrogenation of 1,5-Cyclooctadiene



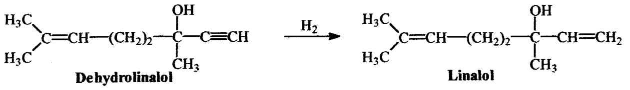
The authors have optimized the hydrogenation reaction of cycloocta-1,3-diene into cyclooctene with Pd colloids[358] or with Pd/Pt bimetallic nanoparticles.[251] The use of a ratio Pd/Pt = 4 led to a 3-fold increase in catalytic activity over the use of Pd monometallic colloids.

Pd/Pt,[254] Au/Pd,[256,281] or Cu/Pt[262] bimetallic colloids stabilized by PVP were also used by Toshima to perform this reaction.

Pd nanoparticles immobilized on resin,[236,358] silica,[226,227,248] or on charcoal[132] were also tested.

III.4.2.2. Selective Hydrogenation of Dehydrolinalol. Linalol is a smelling molecule of the terpene family. It can be obtained by selective hydrogenation of the triple bound of dehydrolinalol into a double bound (Scheme 21).

Scheme 21. Selective Hydrogenation of Dehydrolinalol



This reaction is classically conducted with Pd heterogeneous catalysts. Recently, Pd colloids stabilized by a bloc copolymer (polystyrene-*b*-poly-4-vinylpyridine) and immobilized on alumina were tested as catalyst for this reaction.[359,360] The reaction in toluene at 90 °C and under 1 atm of hydrogen conducted to linalol with a good selectivity of 99.6%.

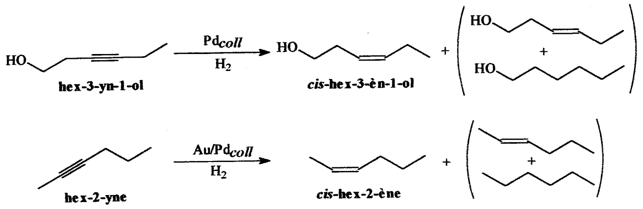
III.4.3. Stereo- and Enantioselective Reactions

Over the past decade, stereo- and mainly enantioselective reactions have been attempted with transition metal colloids. These different studies showed the importance of the protective agent upon the selectivity of these reactions.

III.4.3.1. Stereoselective Hydrogenations. Recently, several examples of stereoselective reduction achieved by metallic colloids were reported in the literature. For example, the selective hydrogenation of alkynes into *cis*-alkenes was studied with transition metal colloids.

Schmid has reported the first unexpected hydrogenation of hex-2-yne into *cis*-hex-2-ene with 90−99% of selectivity. This reaction was catalyzed by Pd colloids immobilized on TiO_2, by Pd colloids stabilized by phenanthrolin,[43,44] or by Au/Pd bimetallic colloids stabilized by TPPTS.[282,283] The use of Pt colloids stabilized by PVP supported on mesoporous solids gave the same results.[361] Following the same procedure, Bönnemann performed the hydrogenation of hex-3-yn-1-ol into *cis*-hex-3-en-1-ol with Pd colloids immobilized on $CaCO_3$. The selectivity obtained was about 98% (Scheme 22).[325,362]

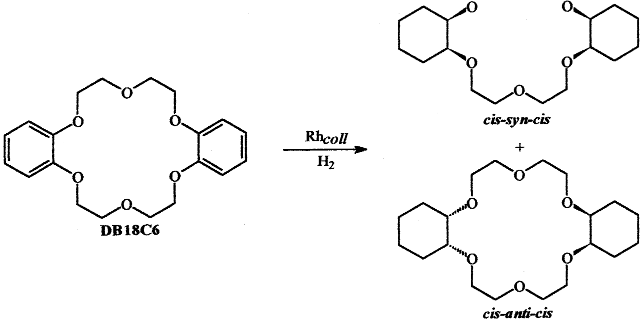
Scheme 22. Stereoselective Hydrogenation of Alkynes



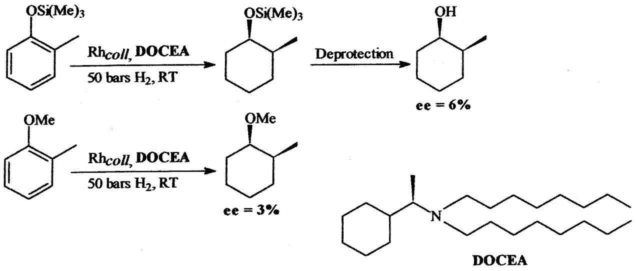
Lemaire has used metallic colloids to carry out the stereoselective hydrogenation of dibenzo-18-crown-6-ether (DB18C6) into dicyclohexano-18-crown-6-ether.[88,89] This reaction was conducted under mild conditions (room temperature, 1 atm of hydrogen) by using Rh nanoparticles stabilized by several amines (trioctylamine, methyltrioctylammonium chloride). The major product is the cis−syn−cis compound (Scheme 23). Nevertheless, the stereoselectivity of the reaction depends on the pressure and on the stabilizing agent used. Thus, a ratio syn/anti = 95/5 can be obtained if the reaction occurs under 50 bar of hydrogen with trioctylamine as stabilizing agent.

III.4.3.2. Enantioselective Hydrogenations. The first example of asymmetric reaction made with colloidal particle was reported by Lemaire and coworkers. They described the hydrogenation of 2-methylanisole or *o*-cresol trimethylsilyl ether. The asymmetric hydrogenation was induced by a chiral amine ((*R*)-dioctylcyclohexyl-1-ethylamine) which was also the protecting agent of the Rh particles (Scheme 24).[90] Nevertheless, ee values obtained were poor (~5%).

Scheme 23. Stereoselective Hydrogenation of DB18C6

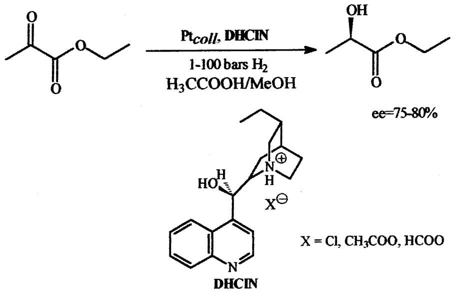


Scheme 24. Enantioselective Reduction of *o*-Cresol



This concept of chiral stabilizing agent has been used by Bönnemann to hydrogenate ethyl pyruvate into ethyl lactate with Pt colloids. The nanoparticles were stabilized by a dihydrocinchonidine salt (DHCIN) and were used in liquid phase or immobilized on charcoal or silica. This system allows the hydrogenation of ethyl pyruvate into (*R*)-ethyl lactate with 75−80% ee (Scheme 25).[362,363]

Scheme 25. Enantioselective Reduction of Ethyl Pyruvate



Recently, other reaction conditions appeared in the literature. Various ee values were stated for the hydrogenation of ethyl pyruvate catalyzed by Pt colloids stabilized by PVP and modified with cinchonidine (ee: 95−98%)[364−366] or catalyzed by solvent-stabilized Pt and Pd nanoparticles prepared by metal vapor synthesis routes (ee: up to 30%).[218] In the last case, Whyman observed a reversed sense of the enantioselectivity (*R*)- vs (*S*)-enantiomer and an acceleration in reaction rate relative to the unmodified system.

III.4.4. Benzene Derivatives Compounds Hydrogenation

The hydrogenation of arene derivatives is an active area of research.[90,367−373] The hydrogenation of benzene to cyclohexane represents an important industrial catalytic transformation, but it is well-known that the hydrogenation of arenes is more difficult to catalyze than the simple olefins. Generally, this reaction is carried out with heterogeneous catalysts,[374−381] but some pure homogeneous systems have been reported.[371,382−386] In few cases, these homogeneous catalysts have been shown to be microheterogeneous catalysts.[21−23,387−389] Consequently, the use of rhodium and ruthenium nanoparticles for arene derivatives hydrogenation has been largely reported.[90,369,387−401] Few examples describe the use of Pd, Pt, and Ni colloids.[89,391,397] Molecular complexes precursors have been used to prepare nanoparticles such as $[RhCl(1,5\text{-hexadiene})]_2$,[390,393−395] $[RhCl(1,5\text{-cyclooctadiene})]_2$,[392,393,396] $[RhH(1,5\text{-cyclooctadiene})]_4$,[392] and $[Rh(OC_6H_5)(1,5\text{-cyclooctadiene})]_2$.[393] The chemical reduction of transition metal salts can be also used such as Pt and Ru sulfite acid solutions,[391] $RhCl_3\ xH_2O$,[88−90,369,387−390,393−395,397−401] K_2PtCl_6,[89] MCl_n (M = Pd, Ni, Ir, and n = 2 or 3),[89,397] $RuCl_3$.[89,369,395,397] The main stabilizers essentially used in the hydrogenation of arene derivatives to prevent colloids from aggregation are tetraalkylammonium salts,[88−90,369,387,393,395−397] polymers,[394] surfactants,[387,398−401] or polyoxoanions.[13,373,402]

Generally, rhodium metal is the most active arene hydrogenation nanocluster catalyst. The reaction conditions are mostly mild (20−50 °C and 1−10 atm H_2) and often performed in biphasic liquid−liquid media. Only one study describes the possibility to use colloids to catalyze hydrogenation of various mono and disubstituted benzene derivatives with an efficient recycling process.[398−401] Recently, a promising partial hydrogenation of anisole to 1-methoxycyclohexene has been obtained by Finke's catalyst. This polyoxoanion-stabilized Rh(0) nanoclusters formed in situ by reducing $[Bu_4N]_5Na_3[(1,5\text{-COD})Rh\cdot P_2W_{15}Nb_3O_{62}]$ with H_2 also shows a catalytic lifetime of 2600 TTO (in 144h), which is the longest demonstrated lifetime for nanoparticle arene hydrogenation catalyst.[373,402]

IV. Conclusion

Presently, numerous methods of preparation of metal colloids are available and they allow one to obtain dispersions containing nanoparticles with a diameter in the 1 to 10 nm range. This degree of dispersion is produced both by a synthetic methodology which makes a quick reduction of metal precursor take place but also by the presence of a stabilizing agent which avoids the formation of metal aggregates. The preparation processes are henceforth modulating according to the type of metal colloids desired. Organic or aqueous suspensions of nanoparticles as well as colloids on solid support are available by the use of stabilizing agents and suitable metal precursors. In the same way, the synthesis of bi- and trimetallic particles is more and more investigated. Moreover, specialized characterizations methods have appeared, and not only the size but also the structure and composition of metal nanoparticles can henceforth be established through further techniques of microscopy, X-ray, or spectroscopy.

The use of new materials has known in the last years a substantial development in the field of catalysis.[13] In fact, nanoparticles suspensions of transition metals have shown efficient activities and selectivities. Particularly important may be studies of enhanced selectivity, activity, and catalytic lifetime of mono- or multimetallic nanoclusters. The mono- or bimetallic colloids are known to be the active species in reactions presumed some years ago to be catalyzed by molecular complexes[403] and are successfully used in an increasing number of reactions. In the main fields of application of homogeneous catalysis, many catalytic reactions such as hydrogenation, oxidation, hydrosilylation, or more recently C−C coupling can be performed now by nanoparticles dispersed in liquid media. Finally, the type of stabilizing agents as polymer, surfactant, polyanion, or ligand has allowed the modulation of the reactivity of these catalytic systems.

Today, the key goal in the transition metal colloid area is the development of reproducible nanoparticles syntheses in opposition to traditional colloids typically larger (>10 nm) and not reproducibly prepared giving irreproducible catalytic activities. Modern nanoclusters should be or have at least (i) specific size (1−10 nm), (ii) well-defined surface composition, (iii) reproducible synthesis and properties, (iv) isolable and redissolvable ("Bottleable") and finally (v) high catalytic activities in solution with long device lifetime with reproducible performance. Morever, development of nanoclusters indifferently used in drastic conditions (higher pressures and temperatures) or not will be also a key in future nanocluster science. We also want to point out the major interest of reusability, which is obviously not systematically studied (or published) in the matal colloid literature.

However, the numerous recent studies show that the use of metal nanoparticles in catalysis is promising provided that the lifetime of these materials is sufficient and that they offer possibilities of recycling. These two properties are essential conditions for industrial applications of these original and powerful catalysts.

V. Acknowledgment

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