Nanoscopic Metal Particles − Synthetic Methods and Potential Applications

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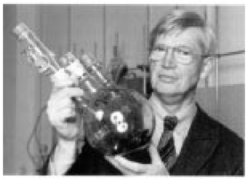
Mono- and bimetallic colloidal particles have gained increasing attention in science and application throughout the last several years. In this contribution, we present a synopsis of the wet chemical syntheses of these materials and survey potential applications in catalysis and materials science. Methods for the characterization of these particles and their surfaces are not reviewed here.

Introduction

Colloidal metals − originally called gold sols − first generated interest because of their intense colors, which enabled them to be used as pigments for glass or ceramics. Nanoparticulate metal colloids are generally defined as isolable particles between 1 and 50 nm in size that are prevented from agglomerating by protecting shells. They can be redispersed in water ("hydrosols") or organic solvents ("organosols"). The number of potential applications of these colloidal particles is growing rapidly because of the unique electronic structure of the nanosized metal particles and their extremely large surface areas. A considerable body of knowledge has been accumulated on these materials over the last few decades.[1−12] Highly dispersed mono- and bimetallic colloids can be used as precursors for a new type of catalyst that is applicable both in the homogeneous and heterogeneous phases.[13−16] Besides the obvious applications in chemical catalysis, recent studies have examined the potential of nanostructured metal colloids as fuel cell catalysts.[17−20]

Wet Chemical Preparations

Nanostructured metal colloids have been obtained by so-called "top-down methods", e.g. by the mechanical grinding of bulk metals and subsequent stabilization of the resulting nanosized metal particles by the addition of colloidal protecting agents.[21−22] Metal vapor techniques have provided chemists with a very versatile route for the production of a wide range of nanostructured metal colloids on a preparative laboratory scale.[23−28] The use of metal vapor techniques is, however, limited because the operation of the apparatus is demanding and it is difficult to obtain narrow particle size distributions. The "bottom-up methods" of wet chemical nanoparticle preparation rely on the chemical reduction of metal salts, electrochemical pathways, or the controlled decomposition of metastable organometallic compounds. A large variety of stabilizers, e.g. donor ligands, polymers, and surfactants, are used to control the growth of the initially formed nanoclusters and to



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MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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prevent them from agglomeration. The chemical reduction of transition metal salts in the presence of stabilizing agents to generate zerovalent metal colloids in aqueous or organic media was first published in 1857 by Faraday[29] and this approach has become one of the most common and powerful synthetic methods in this field.[10,11,30] The first reproducible standard protocols for the preparation of metal colloids (e.g., for 20 nm gold by reduction of $[AuCl_4]^-$ with sodium citrate) were established by Turkevich.[1−3] He also proposed a mechanism for the stepwise formation of nanoclusters based on nucleation, growth, and agglomeration, which in essence is still valid. Data from modern analytical techniques and more recent thermodynamic and kinetic results have been used to refine this model, as illustrated in Figure 1.[31−36]

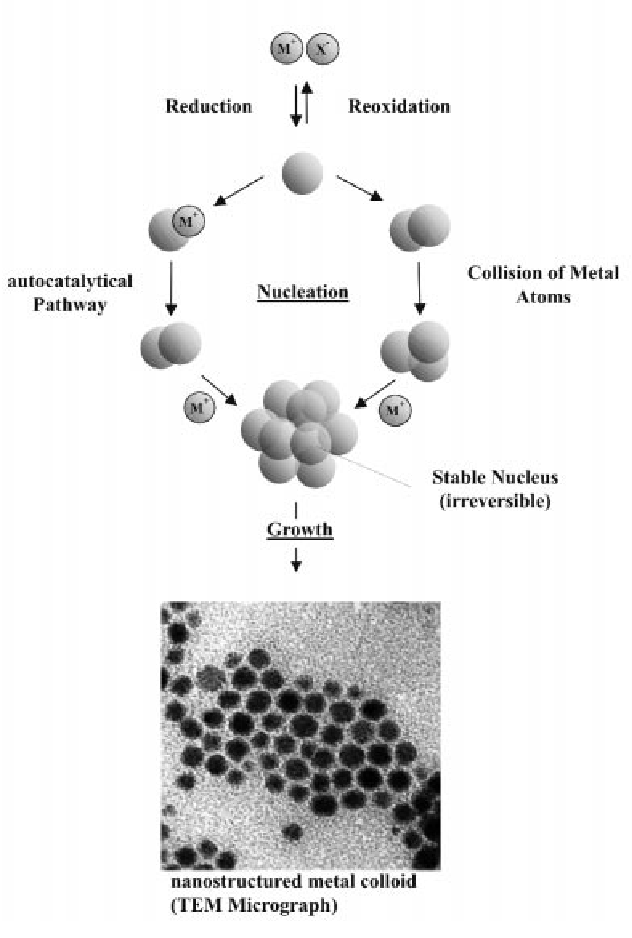


Figure 1. Formation of nanostructured metal colloids by the "salt reduction" method (adapted with permission from ref.[135])

In the embryonic stage of the nucleation, the metal salt is reduced to give zerovalent metal atoms.[31] These can collide in solution with further metal ions, metal atoms, or clusters to form an irreversible "seed" of stable metal nuclei. The diameter of the "seed" nuclei can be well below 1 nm depending on the strength of the metal−metal bonds and the difference between the redox potentials of the metal salt and the reducing agent applied.

Protective agents are necessary to stabilize nanostructured colloidal metals and to prevent agglomeration. Two basic modes of stabilization have been distinguished (Figure 2).[30]

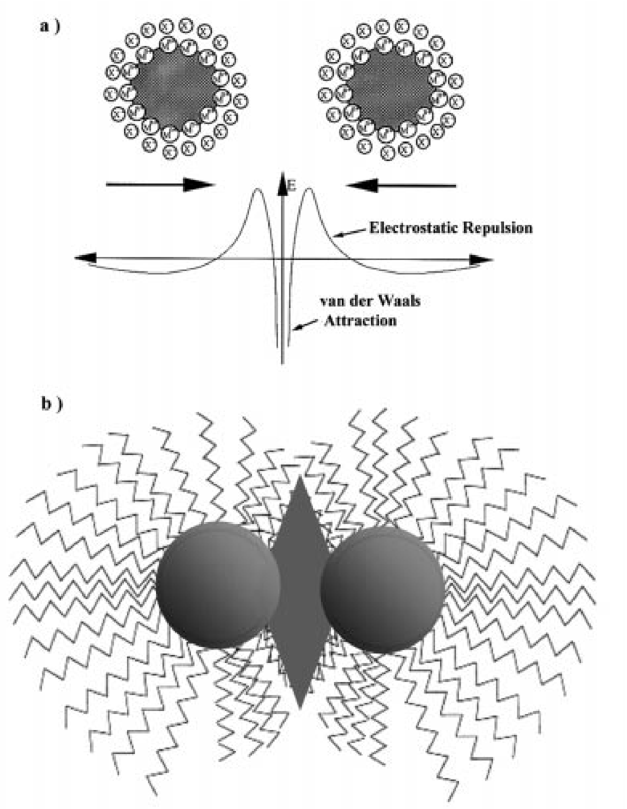


Figure 2. a) Electrostatic stabilization of nanostructured metal colloids (scheme adapted with permission from ref.[30]); b) steric stabilization of nanostructured metal colloids (scheme adapted with permission from ref.[30])

Electrostatic stabilization [see Figure 2, a)] is based on the Coulombic repulsion between the particles caused by the electrical double layer formed by ions adsorbed at the particle surface (e.g. sodium citrate) and the corresponding counterions. This is exemplified by the gold sols prepared by the reduction of $[AuCl_4]^-$ with sodium citrate.[1−3]

Steric stabilization [Figure 2, b)] is achieved by the coordination of sterically demanding organic molecules that act as protective shields on the metallic surface. In this way, nanometallic cores are separated from each other and agglomeration is prevented. The main classes of protective groups selected from the literature are: polymers[37−40] and block copolymers; P, N, and S donors (e.g. phosphanes, amines, thioethers);[6,57−82] solvents such as THF,[6,83] THF/MeOH,[84] and propylene carbonate;[85] long-chain alcohols;[41−56,86] surfactants;[6,7,9,15,16,85,87−98] and organometallics.[99−102] In general, lipophilic protective agents give metal colloids that are soluble in organic media ("organosols"), while hydrophilic agents yield water-soluble colloids ("hydrosols"). In Pd organosols, stabilized by tetra-

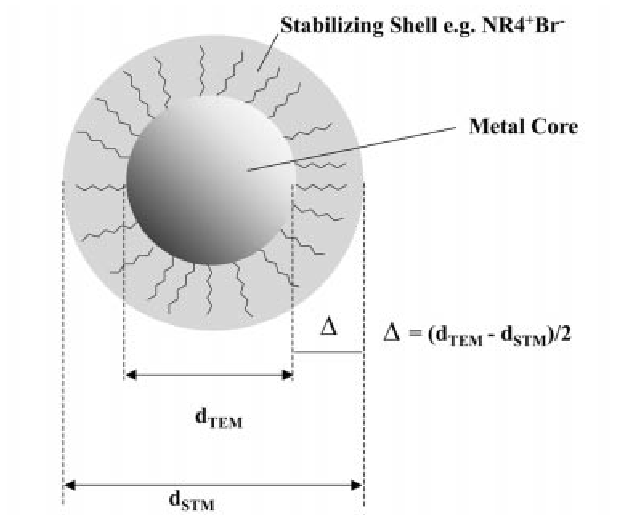


Figure 3. Differential TEM/STEM study of a Pd organosol showing that the metal core (size = d_{TEM}) is surrounded by a monolayer of the surfactant [thickness $\Delta = (d_{\mathrm{TEM}} - d_{\mathrm{STM}})_2$] (adapted with permission from ref.[103])

alkylammonium halides, the metal core is protected by a monolayer of the surfactant coating (Figure 3).[103]

In contrast, metal hydrosols that are stabilized by zwitterionic surfactants capable of self-aggregation are enclosed in organic double layers. After the application of uranyl acetate as a contrasting agent, TEM micrographs show that the colloidal Pt particles (average size 2.8 nm) are surrounded by a double layer zone of the zwitterionic carboxybetaine (3−5 nm). The hydrophilic head group of the betaine interacts with the charged metal surface and the lipophilic tail is associated with the tail of a second surfactant molecule resulting in the formation a hydrophilic outer sphere (see Figure 4).[104] Pt or Pt/Au particles have been hosted in the hydrophobic holes of non-ionic surfactants, e.g. polyethylene monolaurate.[105,106]

Reducing Agents

It has been experimentally verified in the case of silver[31] that stronger reducing agents produce smaller nuclei in the "seed". These nuclei grow during the "ripening" process to yield colloidal metal particles in the size range 1−50 nm, which have a narrow size distribution. The mechanism of particle formation was assumed to involve an agglomeration of zerovalent nuclei in the "seed" or, alternatively, collisions of already formed nuclei with reduced metal atoms. Henglein[32] has monitored the stepwise reductive formation of Ag_3^+ and Ag_4^+ clusters by spectroscopic methods. His results strongly suggest that an autocatalytic pathway is involved, in which metal ions are adsorbed and successively reduced at the zerovalent cluster surface. The formation of colloidal Cu protected by cationic surfactants (NR_4^+) was investigated by in situ X-ray absorption spectroscopy, which revealed the formation of an intermediate Cu^+ state prior to nucleation of the particles.[35] It is now generally accepted that the size of the resulting metal colloid is determined by the relative rates of nucleation and particle growth, although the processes involved in nucleation and particle growth cannot be analyzed separately.

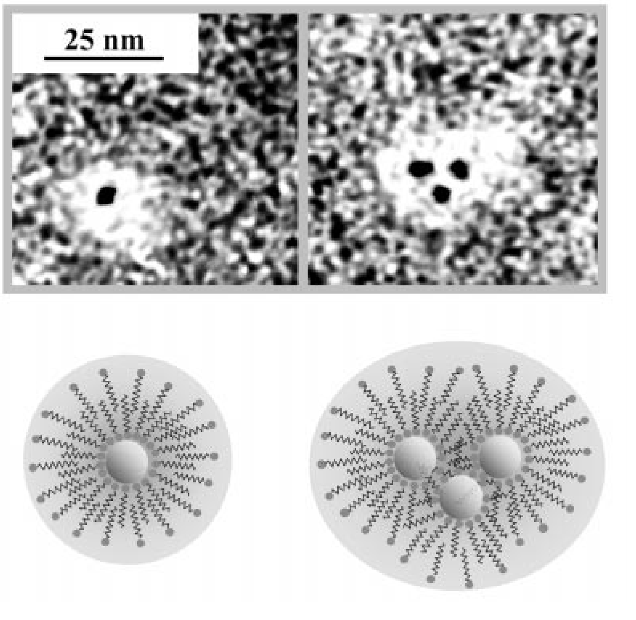


Figure 4. Top: TEM micrographs of colloidal Pt particles (single and aggregated; average core size = 2.8 nm) stabilized by carboxybetaine 12 (3−5 nm, contrasted with uranyl acetate against the carbon substrate); bottom: schematic model of the hydrosol stabilization by a double layer of the zwitterionic carboxybetaine 12 (/\/\/\ = lipophilic alkyl chain; −o = hydrophilic, zwitterionic head group) (adapted from ref.[104])

The main advantages of the salt reduction method in the liquid phase are that it is reproducible and allows colloidal nanoparticles with a narrow size distribution to be prepared on a multigram scale. The classical Faraday route, as in the reduction of $[AuCl_4]^-$ with sodium citrate for example, is still used to prepare standard 20 nm gold sols for histological staining applications.[1,107] Wet chemical reduction procedures have been applied in the last decades to successfully combine practically all transition metals with the different types of stabilizers and the whole range of chemical reducing agents. In 1981, Schmid et al. established the "diborane-as-reductant route" for the synthesis of $Au_{55}(PPh_3)_{12}Cl_6$ (1.4 nm), a full shell ("magic number") nanocluster stabilized by phosphane ligands.[57−71] Clusters of Au_{55} are uniformly formed when a stream of B_2H_6 is carefully introduced into an Au^{III} ion solution. The "diborane route" for $M_{55}L_{12}Cl_n$ nanoclusters was recently reviewed by Finke et al.[11] Bimetallic nanoclusters made accessible by this method[57−71] have been thoroughly characterized. Using silsesquioxanes, the phosphane ligands may be quantitatively exchanged in the Au_{55} nanoclusters, which causes marked changes in the physical and chemical behavior of these clusters.[71] The synthesis and general chemistry of nanosized silica-coated metal particles has been elaborated by Mulvaney.[72] The "alcohol reduction process" of Hirai and Toshima[10,37−40,323,324] is widely applicable for the preparation of colloidal precious metals stabilized by organic polymers such as poly(vinylpyrrolidone) (PVP), poly(vinyl alcohol) (PVA), and poly(methylvinyl ether). Alcohols having α-hydrogen atoms are oxidized to the corresponding carbonyl compound (e.g. methanol to formaldehyde) during the salt reduction. The method for preparing bimetallic nanoparticles by the co-reduction of mixed ions has been evaluated in a recent review.[10] Hydrogen is an efficient reducing agent for the preparation of electrostatically stabilized metal sols and of polymer-stabilized hydrosols of Pd, Pt, Rh, and Ir.[108−112] Moiseev's "giant" palladium cluster [Figure 5, a)][73−78] and Finke's polyoxoanion- and tetrabutylammonium-stabilized transition metal nanoclusters [Figure 5, b)][11,34,113−117] were also prepared by the hydrogen reduction pathway.

The characterization of Moiseev's giant cationic palladium clusters[73−78] [Figure 5, a)] [idealized formula $Pd_{\approx 561}L_{\approx 60}(OAc)_{\approx 180}$ (L = phenanthroline, bipyridine)] and their catalytic properties have recently been reviewed by Finke et al.[11] The results of a combination of modern instrumental analysis methods applied to Finke's nanoclusters were discussed in detail in the same review.[11]

Colloidal Pt in water[2,118] was obtained using CO, formic acid, sodium formate, formaldehyde, and benzaldehyde as reductants.[119] Silanes have been found to be effective for the reductive preparation of Pt sols.[120,121] Duff, Johnson, and Baiker have successfully introduced tetrakis(hydroxymethyl)phosphonium chloride (THPC) as a reducing agent that allows the size- and morphology-selective synthesis of Ag, Cu, Pt, and Au nanoparticles from the corresponding metal salts.[122−127] Furthermore, hydrazine,[128] hydroxylamine,[129] and electrons trapped in, for example, $K^+[(crown)_2K]^-$,[130] have been applied as reductants. In addition, BH_4^- is a powerful and valuable reagent for the salt reduction method. However, a disadvantage is that transition metal borides are often found alongside the nanometallic particles.[131,132] Tetraalkylammonium hydrotriorganoborates[6,7,9,15,87−89] offer a wide range of applications in the wet chemical reduction of transition metal salts. In this case, the reductant $[BEt_3H]^-$ is combined with the stabilizing agent (e.g. NR_4^+). The surface-active NR_4^+ salts are formed immediately at the reduction center in high local concentration and prevent particle aggregation. Trialkylboron is recovered unchanged from the reaction mixture and no borides contaminate the products.

$$MX_\nu + NR_4(BEt_3H) \longrightarrow M_{colloid} + \nu\, NR_4X + \nu\, BEt_3 + \nu/2\, H_2\uparrow \qquad (1)$$

M = metals of groups 6–11; X = Cl, Br; ν = 1–3; R = alkyl, C_6–C_{20}

As synthesized, the NR_4^+-stabilized "raw" metal colloids typically contain 6−12 wt-% of metal. "Purified" transition metal colloids containing ca. 70−85 wt-% of metal are obtained by work-up with ethanol or diethyl ether and subsequent reprecipitation from a solvent of different polarity (see Table 9 in ref.[6]). The pre-preparation of $[NR_4]^+[BEt_3H]^-$ can be avoided if NR_4X is coupled to the metal salt prior to the reduction step. Transition metal nanoparticles stabilized by NR_4^+ can also be obtained from NR_4X/transition metal double salts. A number of conventional reducing agents may be applied since the local concentration of the protecting group is sufficiently high for Equation (2) to hold.[7,15]

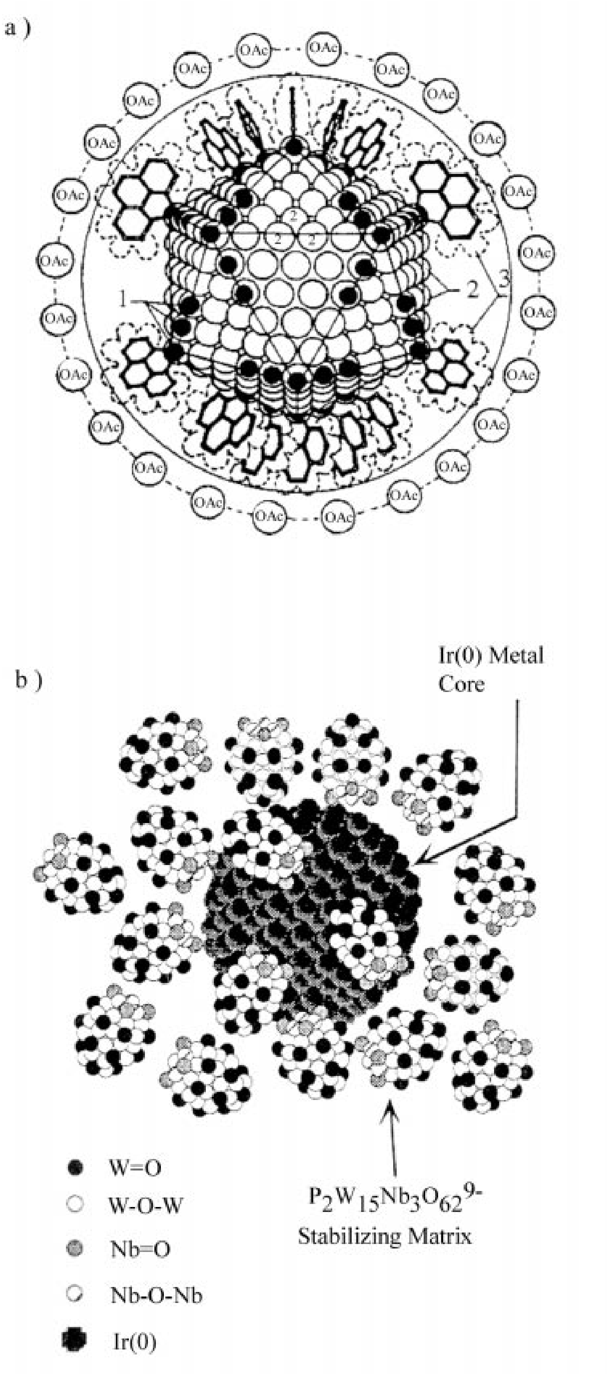


Figure 5. a) Idealized model of Moiseev's "giant palladium cluster" $Pd_{\approx 561}phen_{\approx 60}(OAc)_{\approx 180}$ (phen = phenanthroline) (adapted from ref.[73]); b) idealized model of a Finke-type Ir^0 nanocluster $P_2W_{15}Nb_3O_{62}^{9-}$ and Bu_4N^+-stabilized $Ir^0_{\approx 300}$ (adapted with permission from ref.[113])

$$(NR_4)_wMX_\nu Y_w + \nu\, Red \longrightarrow M_{colloid} + \nu\, RedX + w\, NR_4Y \qquad (2)$$

M = metals; Red = H_2, HCO_2H, K, Zn, LiH, $LiBEt_3H$, $NaBEt_3H$, $KBEt_3H$; X,Y = Cl, Br; ν, w = 1–3; R = alkyl, C_6–C_{12}

Table 1. THF-stabilized organosols of early transition metals

Product	Starting material	Reducing agent	T [°C]	t [h]	Metal content [%]	Size [nm]
[Ti·0.5THF]	$TiBr_4$·2THF	$K[BEt_3H]$	room temp.	6	43.5	(< 0.8)
[Zr·0.4THF]	$ZrBr_4$·2THF	$K[BEt_3H]$	room temp.	6	42	−
[V·0.3THF]	VBr_3·3THF	$K[BEt_3H]$	room temp.	2	51	−
[Nb·0.3THF]	$NbCl_4$·2THF	$K[BEt_3H]$	room temp.	4	48	−
[Mn·0.3THF]	$MnBr_2$·2THF	$K[BEt_3H]$	50	3	70	1−2.5

In a recent review,[11] the scope and limitations of this method were evaluated. Isolable colloids of the zerovalent early transition metals stabilized only by THF have been prepared by $[BEt_3H]^-$ reduction of the preformed THF adducts of $TiBr_4$ [Equation (3)], $ZrBr_4$, VBr_3, $NbCl_4$, and $MnBr_2$. Table 1 summarizes the results. Detailed studies of [Ti·0.5 THF][83] have shown that it consists of Ti_{13} clusters in the zerovalent state, stabilized by six intact THF molecules (Figure 6).

$$x\,[TiBr_4 \cdot 2\,THF + x{\cdot}4\,K[BEt_3H] \xrightarrow{\text{THF, 2 h, 20 °C}} [Ti \cdot 0.5\,THF]_x + x{\cdot}4\,BEt_3 + x{\cdot}4\,KBr\downarrow + x{\cdot}4\,H_2\uparrow \qquad (3)$$

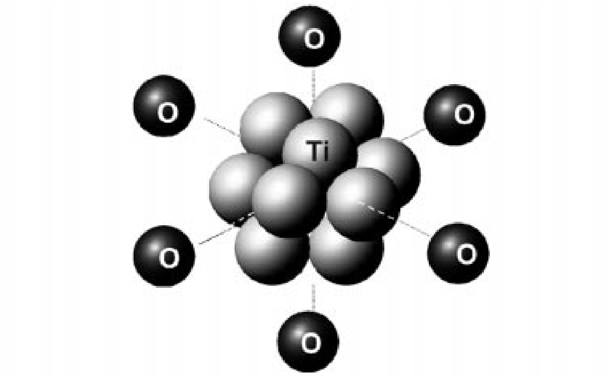


Figure 6. Ti_{13} cluster stabilized by six THF O atoms in an octahedral configuration

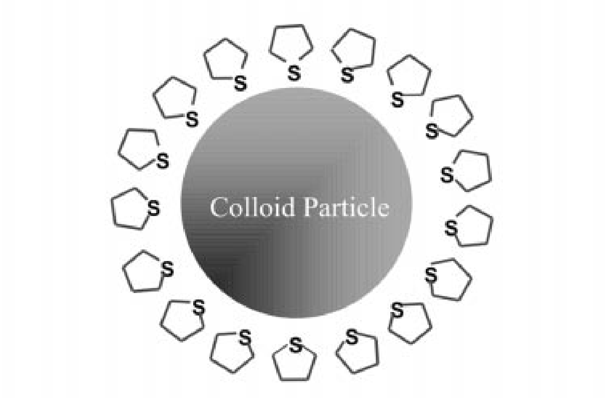


Figure 7. Organosols stabilized by tetrahydrothiophene; M = Ti, V (decomposition); M = Mn, Pd, Pt; stable colloids

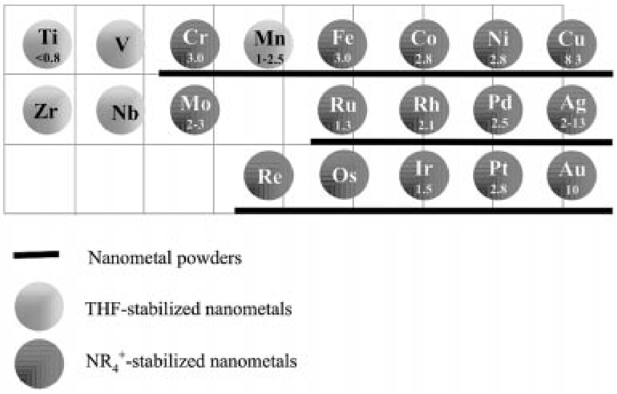


Figure 8. Nanopowders and nanostructured metal colloids accessible by the $[BEt_3H]^-$ reduction method (including the mean particle sizes obtained) (adapted with permission from ref.[7])

By analogy, [Mn·0.3THF] particles (1−2.5 nm) have been prepared[133] and their physical properties have been studied.[134] The THF in Equation (3) has been successfully replaced by tetrahydrothiophene (THT) in the case of Mn, Pd, and Pt organosols, but attempts to stabilize Ti and V in this way led to decomposition (Figure 7).[15] Figure 8 gives a survey of the $[BEt_3H]^-$ method.

The advantages of the method (Figure 8) may be summarized as follows:

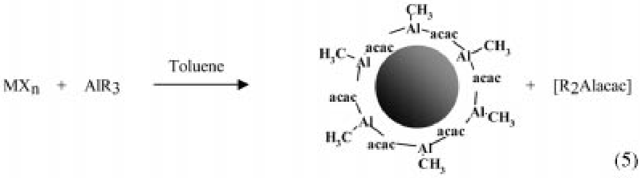
- The method is generally applicable to salts of metals of Groups 4−11 in the Periodic Table.
- It yields extraordinarily stable metal colloids that are easy to isolate as dry powders.
- The particle size distribution is nearly monodisperse.
- Bimetallic colloids are easily accessible by co-reduction of two different metal salts.
- The synthesis is suitable for multigram preparations and is easy to scale up.

One of the drawbacks of this method is that the particle size of the resulting sols cannot be varied by altering the reaction conditions. Highly water-soluble hydrosols, particularly those of zerovalent precious metals, were made accessible by using betaines instead of NR_4^+ salts as the protecting group in Equation (1). A wide variety of hydrophilic surfactants may be used in Equation (2).[7,15,88] Reetz and Maase have reported a new method for the size- and morphology-selective preparation of metal colloids using tetraalkylammonium carboxylates of the type $NR_4^+R'CO_2^-$ (R = octyl; R′ = alkyl, aryl, H) as both the reducing agent and the stabilizer [Equation (4)].[135−137,325]

$$M^+ + R_4N^+\ R'CO_2^- \xrightarrow{50\text{–}90\ °C} M^0(R_4NR'CO_2)_x + CO_2 + R'\text{–}R' \qquad (4)$$

R = octyl, R' = alkyl, aryl, H

The resulting particle sizes were found to correlate with the electronic nature of the R′ group in the carboxylate. Electron donors produced small nanoclusters, whereas electron-withdrawing substituents R′ yielded larger particles. For example, Pd particles of size 2.2 nm were formed when $Pd(NO_3)_2$ was treated with an excess of tetra(*n*-octyl)ammonium carboxylate bearing R′ = $(CH_3)_3CCO_2^-$ (an electron-donating group) as the substituent. With R′ = $Cl_2CHCO_2^-$ (an electron-withdrawing substituent), the particle size was found to be 5.4 nm. Bimetallic colloids of the following were obtained with tetra(*n*-octyl)ammonium formate as the reductant: Pd/Pt (2.2 nm), Pd/Sn (4.4 nm), Pd/Au (3.3 nm), Pd/Rh (1.8 nm), Pt/Ru (1.7 nm), and Pd/Cu (2.2 nm). The shape of the particles was also found to depend on the reductant: With tetra(*n*-octyl)ammonium glycolate and $Pd(NO_3)_2$, a significant amount of trigonal particles was detected in the resulting Pd colloid. Organoaluminum compounds have been used for the "reductive stabilization" of mono- and bimetallic nanoparticles [see Equation (5) and Table 2].[99,100]

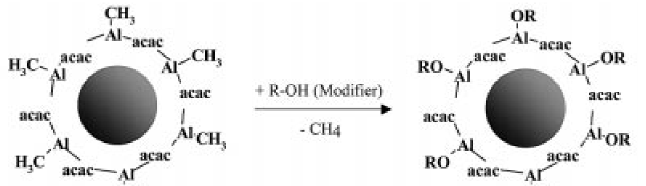


(5)

M = Metals of Groups 6-11 PSE
X = Halogen, Acetylacetonate n = 2-4
R = C_1-C_8-Alkyl
Particle sizes 1-12nm

According to Equation (5), colloids of zerovalent elements of Groups 6−11 of the Periodic Table (and also of tin) may be prepared in the form of stable, isolable organosols. Available analytical data suggest that a layer of condensed organoaluminum species protects the transition metal core against aggregation, as depicted in Equation (5). However, the exact "backbone" of the colloidal organoaluminum protecting agent has not yet been completely established.

Unreacted organoaluminum groups (e.g. $Al-CH_3$, $Al-C_2H_5$) from the starting material are still present in the stabilizer and have been detected by quantitative protonolysis experiments. These active Al−C bonds have been used for a controlled protonolysis by long-chain alcohols or organic acids ("modifiers") to give Al−alkoxide groups in the stabilizer [Equation (6)].



(6)

Modifiers: alcohols, carbonic acids, silanols, sugars, polyalcohols, polyvinylpyrrolidone, surfactants, silica, alumina, etc. (32).

This "modification", Equation (6), of the organoaluminum protecting shell can be used to tailor the dispersion characteristics of the original organosols. A vast spectrum of solubilities of the colloidal metals in hydrophobic and

Table 2. Mono- and bimetallic nanocolloids prepared by the organoaluminum route (see ref.[99])

Metal salt	[g]	[mmol]	Reducing agent	[g]	[mmol]	Toluene [mL]	Conditions *T* [°C]	*t* [h]	Product *m* [g]	Metal content [wt-%]	Particle size *F* [nm]
$Ni(acac)_2$	0.275	1	$Al(iBu)_3$	0.594	3	100	20	10	0.85	Ni: 13.8	2−4
$Fe(acac)_2$	2.54	10	$Al(Me)_3$	2.1	30	100	20	3	2.4	n.d.	
$RhCl_3$	0.77	3.1	$Al(oct)_3$	4.1	11.1	150	40	18	4.5	Rh: 8.5 Al: 6.7	2−3
Ag neodecanoate	9.3	21.5	$Al(oct)_3$	8.0	21.8	1000	20	36	17.1	Ag: 11.8 Al: 2.7	8−12
$Pt(acac)_2$	1.15	3	$Al(Me)_3$	0.86	7.6	150	20	24	1.45	Pt: 35.8 Al: 15.4	2.5
$PtCl_2$	0.27	1	$Al(Me)_3$	0.34	3	125	40	16	0.47	Pt: 41.1 Al: 15.2	2.0
$Pd(acac)_2$ $Pt(acac)_2$	0.54 0.09	1.8 0.24	$Al(Et)_3$	0.46	4	500	20	2	0.85	P: 22 Pt: 5.5 Al: 12.7	3.2
$Pt(acac)_2$ $Ru(acac)_3$	7.86 7.96	20 20	$Al(Me)_3$	8.64	120	400	60	21	17,1	Pt: 20.6 Ru: 10.5 Al: 19.6	1.3
$Pt(acac)_2$ $SnCl_2$	1.15 0.19	2.9 1	$Al(Me)_3$	0.86	12	100	60	2	1.1	Pt: 27.1 Sn: 5.2 Al: 14.4	n.d.

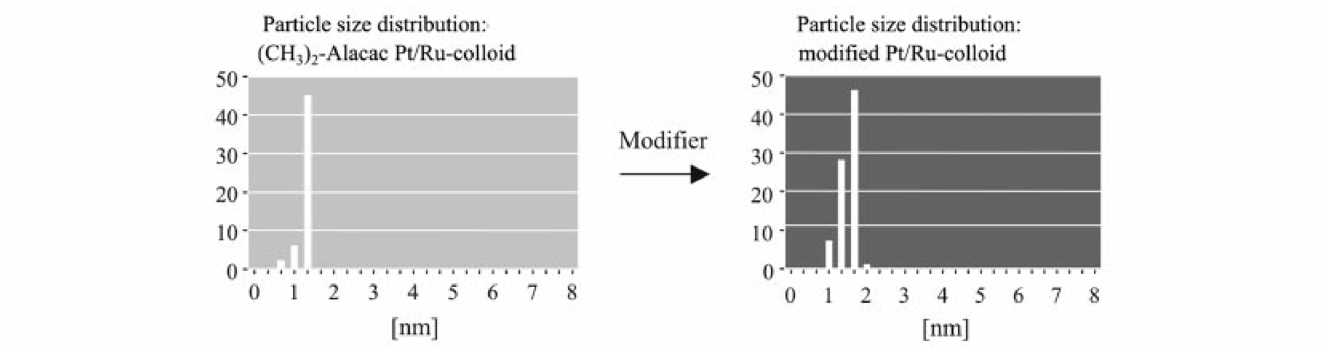


Figure 9. Size conservation of colloidal Pt/Ru particles under the hydrophilic modification of the $(CH_3)_nAl-acac$ protecting shell using polyethylene glycol/dodecyl ether

hydrophilic media (including water) has been achieved in this way. Inorganic surfaces bearing OH groups can react with the active Al−C bonds in the colloidal protecting shell, opening new possibilities for the preparation of heterogeneous catalysts. The modification process does not substantially alter the particle size of the metal core (see Figure 9).[101]

Electrochemical Synthesis

This very versatile means of preparing nanostructured mono- and bimetallic colloids has been further developed by Reetz and his group since 1994.[8,90,91] The overall process of electrochemical synthesis, Equation (7), can be divided into six elementary steps (see Figure 10).

1. Oxidative dissolution of the sacrificial M_{bulk} anode.
2. Migration of M^{n+} ions to the cathode.
3. Reductive formation of zerovalent metal atoms at the cathode.
4. Formation of metal particles by nucleation and growth.
5. Arrest of the growth process and stabilization of the particles by colloidal protecting agents, e.g., tetraalkylammonium ions.
6. Precipitation of the nanostructured metal colloids.

$$\begin{array}{lllll} \text{Anode:} & & M_{bulk} & \rightarrow & M^{n+} + n\,e^- \\ \text{Cathode:} & M^{n+} + n\,e^- + & \text{stabilizer} & \rightarrow & M_{coll}/\text{stabilizer} \\ \hline \text{Sum:} & M_{bulk} + & \text{stabilizer} & \rightarrow & M_{coll}/\text{stabilizer} \end{array} \qquad (7)$$

Advantages of the electrochemical pathway are that contamination with by-products resulting from chemical reducing agents are avoided and that the products are easily isolated from the precipitate. Further, the electrochemical preparation allows for size-selective particle formation. Experiments using Pd as the sacrificial anode in the electrochemical cell to give $(C_8H_{17})_4N^+Br^-$-stabilized Pd^0 particles have indicated that the particle size depends on the current density applied: high current densities lead to small Pd particles (1.4 nm), whereas low current densities give larger particles (4.8 nm).[90] As was seen from a careful analysis of tetraalkylammonium-stabilized Pd and Ni by means of a combination of TEM and SAXS, the control of particle size does not have a single cause. It can be brought about by adjusting the following parameters:

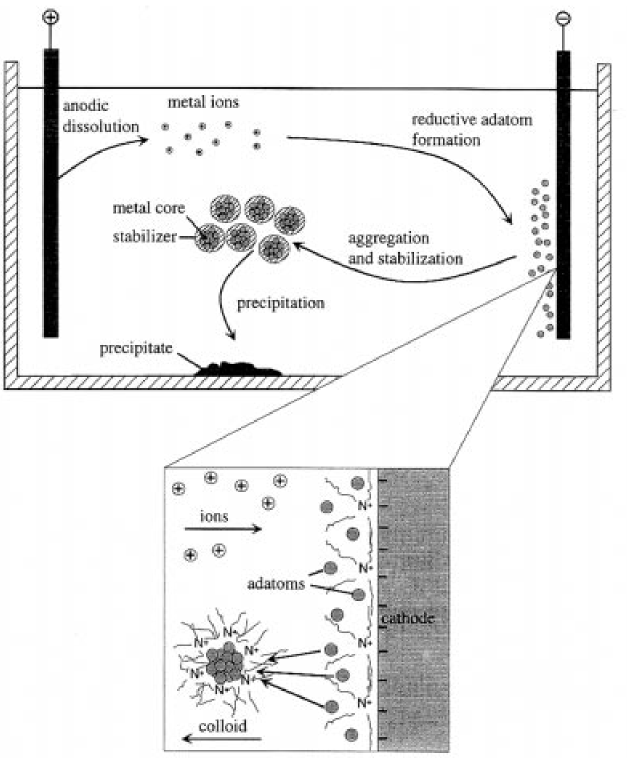


Figure 10. Electrochemical formation of $NR_4^+Cl^-$-stabilized nanometal (adapted with permission from ref.[8])

− the distance between the electrodes,
− the reaction time and temperature,
− the polarity of the solvent.

Nearly monodisperse Pd^0 particles with sizes of 1−6 nm can be obtained by means of electrochemical synthesis. It was also shown that the size of NR_4^+-stabilized Ni^0 particles[92] can be adjusted at will. The electrochemical method[90−97] [Equation (7)] has been successfully applied in the preparation of a number of monometallic organosols and hydrosols, e.g. of Pd, Ni, Co, Fe, Ti, Ag, and Au, on a scale of several hundred milligrams (yields > 95%). Using the electrochemical pathway, solvent-stabilized (propylene carbonate) palladium particles (8−10 nm) have also been obtained.[85] Bimetallic nanocolloids (Pd/Ni, Fe/Co, Fe/Ni) are accessible[95] if two sacrificial M_{bulk} anodes are used in a single electrolysis cell. In the case of Pt, Rh, Ru, and Mo, which are anodically less readily soluble, the corresponding metal salts were electrochemically reduced at the cathode (see bottom part of Figure 10 and Table 3). Tetraalkylammonium acetate has been used as both the supporting electrolyte and the stabilizer in a Kolbe electrolysis at an anode [see Equation (8)].[96] By combining the electrochemical methods described in Equation (7) and Equation (8), bimetallic nanocolloids can be prepared (see Table 4).[96]

$$\begin{array}{lll} \text{Cathode:} & Pt^{2+} + 2\,e^- & \longrightarrow Pt^0 \\ \text{Anode:} & 2\,CH_3CO_2^- & \longrightarrow 2\,CH_3CO_2 + 2\,e^- \end{array} \qquad (8)$$

Table 3. Electrochemical colloid synthesis

Metal Salt	*d* [nm]	EA[a]
$PtCl_2$	2.5[b]	51.21% Pt
$PtCl_2$	5.0[c]	59.71% Pt
$RhCl_3H_2O$	2.5	26.35% Rh
$RuCl_3H_2O$	3.5	38.55% Ru
$OsCl_3$	2.0	37.88% Os
$Pd(OAc)_2$	2.5	54.40% Pd
$Mo_2(OAc)_4$	5.0	36.97% Mo
$PtCl_2 + RuCl_3H_2O$	2.5	41.79% Pt + 23.63% Rh[d]

[a] Based on stabilizer-containing material. − [b] Current density: 5.00 mA/cm². − [c] Current density: 0.05 mA/cm². − [d] Pt−Ru dimetallic cluster.

Table 4. Bimetallics prepared electrochemically

Anode	Metal salt	*d* [nm]	Stoichiometry (EDX)
Sn	$PtCl_2$	3.0	$Pt_{50}Sn_{50}$
Cu	$Pd(OAc)_2$ [a]	2.5	$Cu_{44}Pd_{56}$
Pd	$PtCl_2$	3.5	$Pd_{50}Pt_{50}$

[a] Electrolyte: 0.1 M $[(n\text{-octyl})_4N]OAc$/THF.

By modifying the electrochemical method, the synthesis of layered bimetallic nanocolloids (e.g. of Pt/Pd) has been achieved.[92,97] A preformed $(Oct)_4NBr$-stabilized Pt colloid core (size 3.8 nm) was electrolyzed in 0.1 M $(Oct)_4NBr$ solution in THF with Pd as the sacrificial anode (Figure 11). The preformed Pt core may be regarded as a "living-metal-polymer", on which the Pd atoms are deposited to give "onion-type" bimetallic nanoparticles (5 nm).

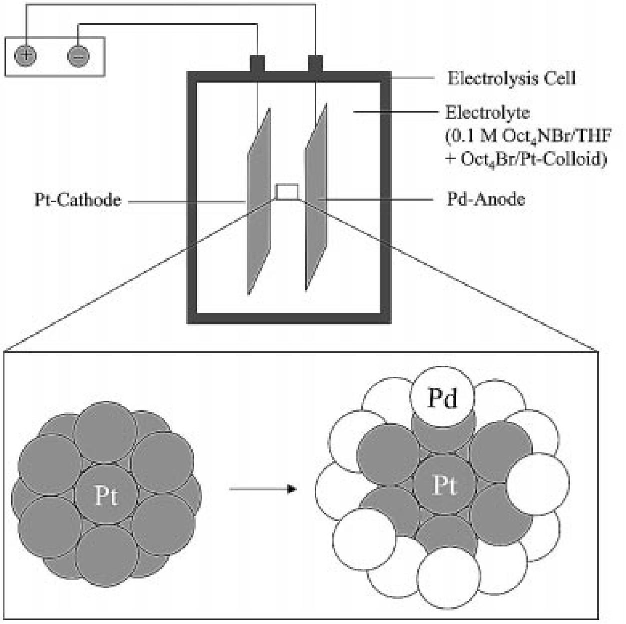


Figure 11. Modified electrolysis cell for the preparation of layered bimetallic Pt/Pd nanocolloids (adapted with permission from ref.[92])

Decomposition of Low-Valent Transition Metal Complexes

Low-valent organometallic complexes and several organic derivatives of the transition metals decompose under the action of heat, light, or ultrasound to give short-lived nucleation particles of zerovalent metals in solution, which may be stabilized by colloidal protecting agents. For example, thermolysis[138−143] leads to the rapid decomposition of carbonylcobalt complexes to give colloidal cobalt in organic solutions.[138,139] Thermolysis of labile precious metal salts in the absence of stabilizers yields colloidal Pd, Pt, and bimetallic Pd/Cu nanoparticles[140] with broad size distributions. These results were found to be greatly improved when the thermolysis was performed in the presence of stabilizing polymers, such as PVP.[141] Recently, heating in a simple household microwave oven has been proposed as a means of preparing nanosized metal particles and colloids.[142,143,326] The substrate is heated uniformly by the electromagnetic waves, leading to a more homogeneous nucleation and a shorter aggregation time. It is informative to compare the particle size of polymer-stabilized Pt colloids (spheres, 2−4 nm, narrow size distribution) prepared by dielectrical microwave heating with that of samples prepared by conventional heating under otherwise identical

Table 5. Comparison of conventional and microwave heating

No.[a]	PVP[b]	NaOH[b]	Average diameter [nm]	Standard deviation [nm]	Relative standard deviation
1	10	0	3.8	0.57	0.15
2	20	0	3.4	0.56	0.16
3	50	0	3.0	0.50	0.17
4	100	0	2.9	0.47	0.16
5	50	2	3.0	0.49	0.16
6	50	4	2.6	0.48	0.18
7	50	6	1.9	0.33	0.17
8	50	8	2.0	0.32	0.16
9	50	10	2.1	0.40	0.19
10	50	0	3.1	1.08	0.35
11	50	8	1.8	0.55	0.31
12	50	0	2.7	0.74	0.27
13	50	8	1.1	0.31	0.28

[a] Nos. 1−9 were prepared by microwave dielectric heating without stirring; nos. 10 and 11 were prepared without stirring, and nos. 12 and 13 were prepared by stirring in a heated oil bath. − [b] The data in the columns labeled PVP and NaOH refer to the molar ratios of PVP (as a monomeric unit) and NaOH to Pt.

conditions (Table 5). Sonochemical decomposition methods have been successfully developed by Suslick[144] and Gedanken[145−147] and have yielded Fe, Mo_2C, Ni, Pd, and Ag nanoparticles in various stabilizing environments.

Isolable colloidal products can be prepared in multigram amounts by the controlled chemical decomposition of zerovalent transition metal complexes by the addition of CO or H_2 in the presence of appropriate stabilizers.[79−82,148−158] Bradley and Chaudret[79−82,149−155,327−333] have demonstrated the use of low-valent transition metal olefin complexes as a very clean source for the preparation of nanostructured mono- and bimetallic colloids. Nanoparticulate colloids have also been successfully prepared in micelles, inverse micelles, and by encapsulation.[32,33][86] Although beyond the focus of this article, we should also mention that a number of nanoparticulate metal oxide systems have been successfully developed.[7,157−162]

Particle Size Control

Metal colloid sols are generally described as "monodisperse" when the particle size deviates by less than 15% from the average value. Histograms with a standard deviation σ from the mean particle size of approximately 20% are described as showing a "narrow size distribution". The kinetics of the particle nucleation from atomic units and of the subsequent growth process cannot be directly observed by physical methods. In practice, the means available to the preparative chemist for controlling the particle size are size-selective separation[43,163,164] and size-selective synthesis.[41−56,90,135−137,165−181]

The so-called *size-selective precipitation* (SPP) method was predominantly developed by Pileni.[42,334] Monodisperse silver particles (2.3 nm, σ = 15%) are precipitated from a polydisperse silver colloid solution in hexane by adding pyridine in three iterative steps. Schmid has recently reported the two-dimensional "crystallization" of truly monodisperse Au_{55} clusters.[163] Schmid has also shown that the size of nanoparticles can be limited by steric restrictions imposed by a 3D polymer network.[335] Chromatographic separation methods proved unsuccessful because the colloid was decomposed after the colloidal protecting shell had been stripped off.[135] Colfen has developed the size-selective ultra-centrifuge separation of Pt colloids.[164] However, although this elegant separation method gives truly monodisperse metal colloids, as yet it can only provide milligram-scale samples. Turkevich was the first to describe size-selective colloid synthesis.[1,2] Using the salt reduction method, he was able to vary the particle size of colloidal Pd between 0.55 and 4.5 nm. The crucial parameters were the amount of reducing agent applied and the pH of the medium. According to the literature concerning the process of nucleation and particle growth, the essential factors that control the particle size are the strength of the metal−metal bond;[40] the molar ratio of metal salt; colloidal stabilizer; and reducing agent;[1,119,126,165−182] the extent of conversion or the reaction time;[119] the applied temperature;[1,166,178] and the pressure.[166] The preparation of nearly monodisperse nanostructured metal colloids using the salt reduction pathway is well documented in the literature. In practice, however, the "control", i.e. the variation of particle sizes (and shapes), in wet chemical colloid synthesis is left to the intuition of the chemist. Recently, Pileni has also demonstrated that control of particle size and composition can be achieved using oil-in-water micelles.[336] At present, the electrochemical synthesis of Reetz and co-workers offers the most rational method for selecting the particle size. Using variable current densities and making appropriate adjustments of further key parameters, these authors have been able to obtain at will almost monodisperse samples of colloidal Pd and Ni with sizes between 1 and 6 nm.[90−97] In the thermal decomposition method, the particle size obtained depends on the heat source (see Table 5).[143] Size control has also been reported for the sonochemical decompositon method and γ-radiolysis.[183,184]

The domain of preparation methods using constrained environments offers control over the metal particle shape by predetermining the size and morphology of the products in nanoscale reaction chambers.[41−56] The controlled temperature-induced size and shape manipulation of 2−6 nm gold particles encapsulated in alkanethiolate monolayers[54] has recently been reported. The use of near-IR laser light has led to an enormous increase in the size of thiol-passivated gold particles up to ca. 200 nm.[54] A new medium-energy ion-scattering (MEIS) simulation program has successfully been applied in analyzing the composition and average particle size of Pt/Rh/α-Al_2O_3.[55]

Applications in Catalysis

"Quasi-Homogeneous" Reactions

Lipophilic or hydrophilic nanostructured metal colloids, dissolved in the form of organosols or hydrosols, can serve as catalysts in organic solutions and in the aqueous phase, respectively. Schmid[64] has referred to these quasi-homogeneous catalytic reactions, which involve solvated metal atom dispersions (SMAD),[26] as "heterogeneous catalysis in solution". Rhodium hydrosols, dissolved in water, were shown to be effective as hydrogenation catalysts in two-phase systems, where the olefin formed the organic phase.[185] Aqueous solutions of Moiseev's giant Pd colloids [Figure 5, a)][73−78] were shown to catalyze a number of reactions in the "quasi-homogeneous" phase, namely oxidative acetoxylation reactions,[73] the oxidative carbonylation of phenol to diphenyl carbonate,[186] the hydrogen-transfer reduction of multiple bonds by formic acid,[187] the reduction of nitriles and nitroarenes, and acetal formation,[188] all with high turnover frequencies and significant lifetimes (see ref.[11]). Remarkable catalytic lifetimes for polyoxoanion- and tetrabutylammonium-stabilized transition metal nanoclusters have been reported by Finke[113−117] (see Figure 5). For example, in the catalytic hydrogenation of cyclohexene, a common test for structure-insensitive reactions, the Ir^0 nanocluster[34] showed up to 18,000 total turnovers with turnover frequencies of 3200 h^{-1}.[189] Recently, as many as 190,000 turnovers were reported in the case of the Rh^0 analogue.[190] These results are quite unprecedented. Obviously, the polyoxoanion component prevents the precious metal nanoparticles from aggregating so that the active metals have high effective surface areas.[190] A recent review[7] compares this new approach with the catalytic properties of other nanometallic systems active in the "quasi-homogeneous" phase. When nanostructured Ti colloids (3 nm), stabilized by Bu_4NBr, were used, the formation of olefins from aldehydes and ketones through McMurry-type coupling reactions was observed.[191] THF-protected Ti_{13} nanoclusters[83] were found to hydrogenate Ti and Zr sponges in the "quasi-homogeneous" phase.[192,193] Using cinchonidine-stabilized Pt colloids, the enantioselective hydrogenation of ethyl pyruvate in HOAc/MeOH solution was performed.[177] Heck and Suzuki C−C bond coupling reactions were catalyzed by $NR_4^+X^-$-stabilized Pd and Pd/Ni colloids in dimethylacetamide. The same reactions have been observed using solvent-stabilized Pd particles in propylene carbonate as the catalyst.[85,194,195] Nanosized Pd colloids generated in situ by the reduction of Pd^{II} to Pd^0 are involved in the catalysis of phosphane-free Heck and Suzuki reactions.[196] Hexagonal or quasi-two-dimensional Pd nanoparticles (*hcp* structure, 53 nm) encapsulated in graphite have also been tested as catalysts for the Heck reaction. Microphotographs confirmed that the nanoparticles were located between the spacing layers of graphite. The catalyst is very stable: Although no strong interaction is present between the nanoparticles and the carbon lattice, the particles cannot be washed out and they are still found inside the carbon lattice after the Heck reaction.[197] The [3+2] cycloaddition of methylenecyclopropane to methyl acrylate is effectively catalyzed by nanostructured nickel colloids (2.5 nm) in solution.[198] The liquid-phase hydrogenation of isomeric undecenoic acids has been shown to be selectively catalyzed by Pt colloids encapsulated in polymerized micelles.[199] Metal colloids stabilized by amphiphilic block copolymers have been used as efficient catalysts in the "quasi-homogeneous" phase.[200−203] A generally applicable synthesis of metal colloids in microemulsions, in particular of nanostructured noble metals in amphiphilic block copolymers, has been devised by Antonietti and coworkers.[200][201] Micelles incorporating nanosized metals are very stable; they undergo no significant change of their colloidal properties such as size and polydispersity and are consequently effective hydrogenation catalysts. The morphology of the metal core can be varied between a "cherry"-type and a "raspberry"-type architecture depending on the strength of the reducing agent. Block copolymer stabilized Pd "raspberry" colloids have an extraordinarily high metal surface area and no additional support is needed for catalytic applications in solution. This type of colloid catalyst combines the advantages of homogeneous and heterogeneous catalysis, i.e. the high selectivity and reactivity of homogeneous hydrogenation catalysts is coupled with the long-term stability of heterogeneous systems. Nanostructured metal colloids, stabilized with synthetic polymers,[204−208] may be regarded as artificial enzyme models. The interaction between the "polymeric fields" and the reactive substrates determines the selectivity of the colloidal nanometal catalysts. Coordinating polymers such as poly(*N*-vinyl-2-pyrrolidone) have been shown to protect nanostructured mono- and bimetallic particles having an average diameter of ca. 1−3 nm and a narrow size distribution.[346−349] The resulting materials have proved to be effective catalysts for olefin hydrogenation,[205] nitrile hydration,[206] and photoinduced electron transfer.[207] The application of dendrimer-encapsulated Pd nanoparticles to fluorous phase soluble catalysts has recently been described.[208] The scope of ligand-stabilized transition metal nanoparticles in catalysis has recently been summarized by Schmid.[68,209]

Heterogeneous Reactions

Heterogeneous catalysts are obtained by depositing preprepared nanometal colloids on supports.[2] On this basis, the so-called "precursor concept" for the manufacture of heterogeneous metal colloid catalysts was developed in the 1990s.[6,7,9,15,87−89] As a result, so-called *egg shell* catalysts were obtained, which contain the active metal particles as a thin layer (< 250 nm) on the surface of the support. Metal colloid catalysts of this type have been successfully applied in the hydrogenation of C−C double bonds, organic carbonyl groups, unsaturated C−N bonds, and in the reduction of N−O bonds.[210] An obvious advantage of the precursor concept over the conventional salt-impregnation method is that both the size and the composition of the colloidal metal precursors may be tailored independently of the support. Furthermore, the metal particle surface may be modified by lipophilic or hydrophilic protective shells and coated by intermediate layers, e.g., of oxide. The modification of the precursor by dopants is also possible. Such catalysts are manufactured by dipping the supports into organic or aqueous media containing the dispersed precursor at ambient temperature to adsorb the pre-prepared particles. This has been demonstrated for supports such as charcoal, various oxidic support materials, and even low-surface-area materials such as sapphire, quartz, and highly oriented pyrolitic graphite (HOPG), for which no subsequent calcination is required (see Figure 12). Researchers at Degussa have demonstrated the feasibility of preparing catalysts for industrial purposes in this way.

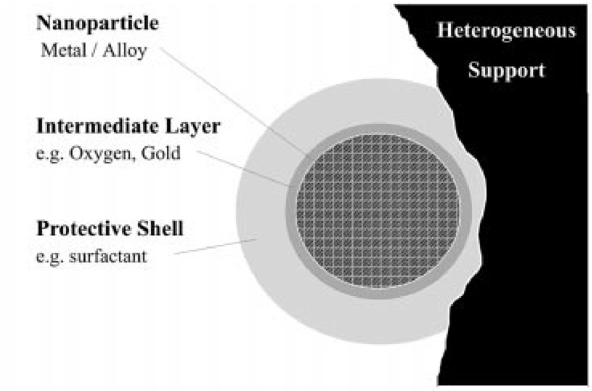


Figure 12. The precursor concept (adapted from ref.[7])

A combination of AFM, STM, and XPS[185] has been used to probe the interaction of platinum hydrosols with oxide (sapphire, quartz) and graphite single-crystal substrates (Figure 13). When dipped into aqueous Pt colloid solutions at 20 °C, the metal core is immediately adsorbed onto the support surface. The carpet-like coating formed over the particles by the protecting shell and the support surface cannot be removed from the particle surface even by repeated washing with solvents. The organic protecting shell decomposes on annealing at 280 °C and above in UHV. By monitoring the thermal degradation up to 800 °C by XPS and STM, it was shown that the Pt particles remain virtually unchanged up to ca. 800 °C, above which sintering processes take place.

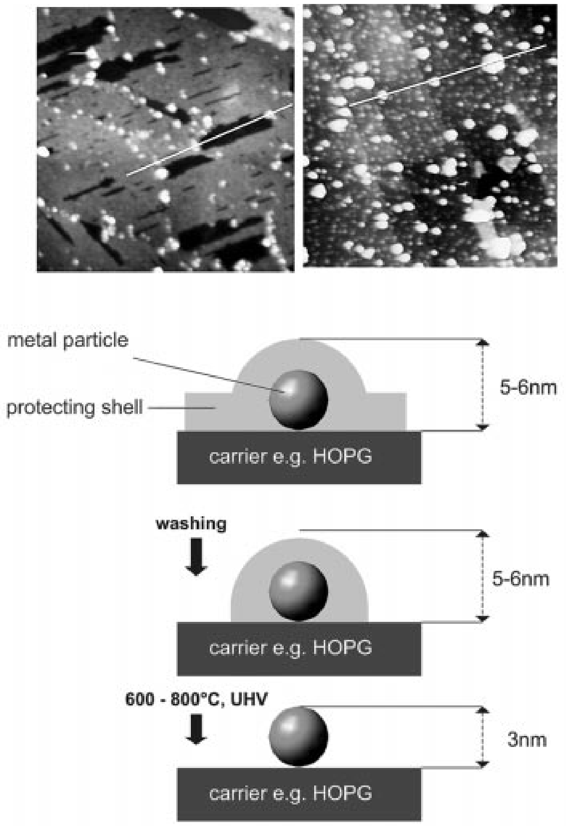


Figure 13. Top: AFM investigation of a sulfobetaine-12 stabilized Pt hydrosol (3 nm) absorbed on highly oriented pyrolytic graphite (HOPG) after dipping (left) and after additional washing (right); bottom: scheme of the Pt hydrosol adsorbtion on HOPG derived from a combined STM and XPS study (ref.[212])

Reetz et al. have used $(\mathrm{octyl})_4\mathrm{NBr}$-stabilized Pd colloids (of typical size 3 nm) as precursors of so-called "*cortex catalysts*", where the active metal forms an extremely fine shell less than 10 nm thick on the support (e.g. $\mathrm{Al_2O_3}$).[213] The impregnation of $\mathrm{Al_2O_3}$ pellets by dispersed nanostructured metal colloids occurs with a time-dependent penetration of the support over the first 1−4 s, and is complete after 10 s [see Figure 14, a)−c)].

"*Cortex catalysts*" were reported to exhibit a threefold higher activity in olefin hydrogenation than conventionally prepared catalysts of the same metal loading (5% Pd on $\mathrm{Al_2O_3}$). Schmid[64] has described phosphane-stabilized $\mathrm{Rh_{55}}$ nanoclusters, namely $\mathrm{Rh_{55}[P(\mathit{t}Bu)_3]_{12}Cl_{20}}$ and $\mathrm{Rh_{55}(PPh_3)_{12}Cl_{20}}$, which were deposited on $\mathrm{TiO_2}$. These systems were reported to catalyze the heterogeneous hydroformylation of propene with high turnover numbers giving equal amounts of *n*- and *iso*-butanal. Although the observed turnover frequencies were higher than those seen with homogeneous complex catalysts, the selectivity was found to be too low for practical applications. In the butyronitrile hydrogenation test, the activity of surfactant-stabilized colloidal rhodium (5 wt-% on charcoal) was found to surpass that of conventional salt impregnation catalysts

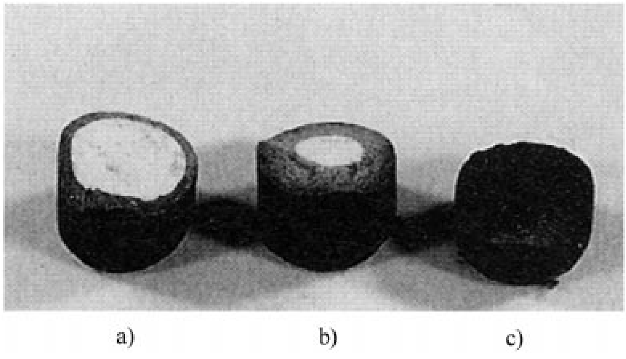


Figure 14. Heterogeneous Pd colloid catalysts of the *cortex*-type (adapted with permission from ref.[213]): a) Al_2O_3 pellets (3.2 mm) after penetration with a 0.5 M solution of $(octyl)_4NBr$-stabilized colloidal Pd in THF for 1 s, b) for 4 s, c) for 10 s

of the same metal loading. The addition of 0.2% colloidal Ti^0 to the supported noble metal[83] resulted in a significant enhancement of the activity (see Figure 15).[7]

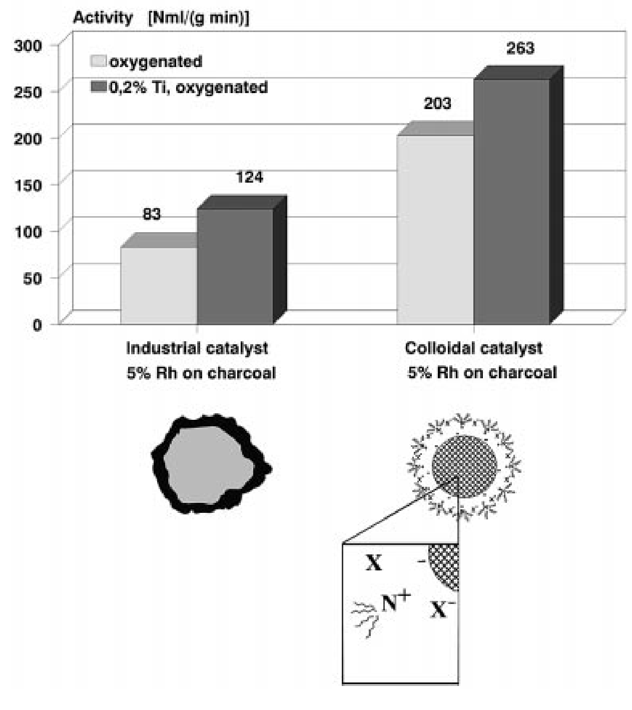


Figure 15. Activities of conventional and colloidal Rh/C catalysts, eventually doped with 2% colloidal Ti^0, compared in the butyronitrile hydrogenation test (adapted with permission from ref.[15])

The compounds used as dopants are not limited to those of the early transition metals. The addition of neodymium ions to the palladium particles was found to have a significant promoting effect on the hydrogenation of acrylic acid.[214] The selective transformation of 3,4-dichloronitrobenzene to the corresponding aniline has been selected to test pre-prepared Pt hydrosols as heterogeneous catalyst precursors (see Figure 16).[215]

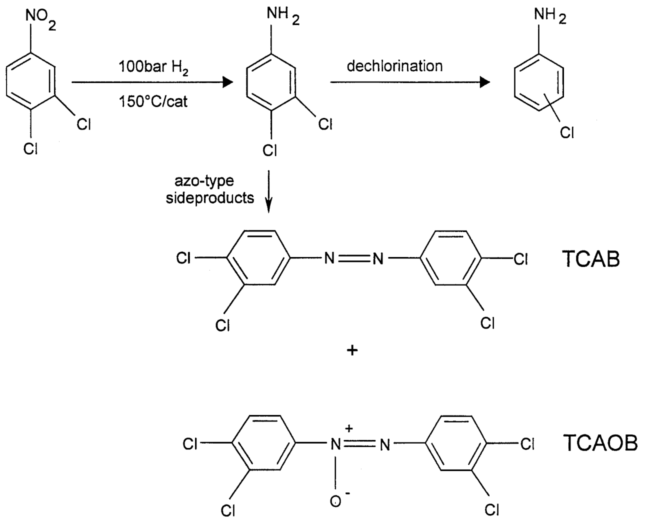


Figure 16. Reaction scheme for the hydrogenation of 3,4-dichloronitrobenzene

The performance of the colloidal catalyst system was evaluated in both batch and continuous tests and compared to that of conventional Pt/C systems. In summary, the potential of the colloidal heterogeneous catalyst stems from the fact that it is possible to tailor the properties for specific applications by the addition of specific dopants or "poisons" (such as sulfur). Further "fine tuning" of the complex process has been achieved by using the synergistic effect of bimetallic precursors (e.g. Pt/Cu). The influence of metal ions on the hydrogenation of *o*-chloronitrobenzene on platinum colloids and the effect of metal complexes on the catalytic performances of metal clusters have also been investigated.[216−218] It was found that the catalytic properties of platinum clusters for the hydrogenation of *o*-chloronitrobenzene to *o*-chloroaniline are very sensitive to the metallic cations added. Enhanced activity and selectivity was observed when Ni^{2+} ions were used as the modifier. The selectivity in the formation of *o*-chloroaniline increased from 44.7% to 66.3%, while the activity of the catalyst was almost doubled. The maximum activity and selectivity (82.9%) in the formation of *o*-chloroaniline was obtained with an Ni^{2+}/Pt molar ratio of 8:1.[216] The same authors also studied the "doping effect" of additional metal complexes on the activity and selectivity of platinum clusters in the homogeneous liquid-phase hydrogenation of cinnamaldehyde.[218] The conversion was increased from 65.5% to 78.0% by using Na_3FeF_6 as the additive, while the selectivity of cinnamic alcohol formation was increased from 17.7% to 75.0%. The addition of $Ni(bipy)_3Cl_2$ to the colloidal platinum catalyst increased the conversion to 82.1%, while the selectivity in the formation of hydrocinnamaldehyde was as high as 97.3%. By doping Rh colloid catalysts with Sn, it was found that the selectivity in the hydrogenation of cinnamic acid to cinnamic alcohol could be varied. A selectivity of 86% was achieved using a colloidal Rh/Sn (Rh/Sn = 1.5:1) catalyst on carbon.[15] Remarkably, the stabilizing surfactant was shown to modify the colloidal metal surface and hence the catalytic properties.[215] Hanaoka et al.[219] have reported the selective photocatalytic transfer of hydrogen to 1,5-cyclooctadiene using a light transition metal modified rhodium colloid catalyst. Bulk industrial processes often rely on alloy-like bimetallic catalysts.[220−222] Here, nanostructured bimetallic colloid catalysts have provided a possibility of carrying out differential studies on the mutual influence of two different metals on the catalytic properties. The controlled co-reduction of two different metal ions has made bimetallic colloids readily accessible.[6,7,15,37−40,69,85,90−97,223] The structural characterization and some catalytic aspects of bimetallic colloids have recently been reviewed.[10] The successive reduction of different metal ions allows the homogeneous structure of bimetallic particles to be altered to one of colloidal particles having composition gradients from the core to the shell.[205,224−227] Truly layered particles consisting of, for example, a gold core plated by palladium or vice versa,[69] have also been synthesized. Bimetallic particles having a gradient metal distribution or a layered structure are most interesting for catalytic applications. In the catalytic hydrogenation of crotonic acid to give butanoic acid, a clear synergistic effect of Pt and Rh[6] was observed using bimetallic colloidal precursors ($Pt_{20}Rh_{80}$) having a gradient core/shell structure with an increase in the Rh content on going from the core to the surface of the particle (see Figure 17).[224] Toshima has discussed a similar effect in the partial hydrogenation of 1,3-cyclooctadiene with $Pt_{80}Pd_{20}$ and $Pd_{80}Au_{20}$ colloid catalysts.[10]

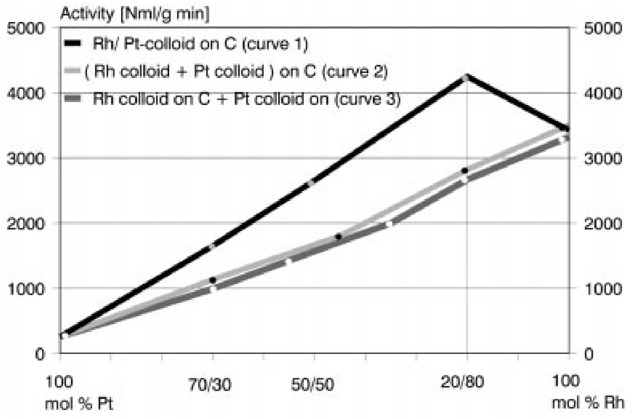


Figure 17. Activity plot of alloyed Rh/Pt/C and mixed Rh + Pt/C catalysts in the crotonic acid hydrogenation test (H_2 consumption) (adapted with permission from ref.[15])

The difference in the electronegativities of Pd and Au, together with the combination of the partially filled d band of Pd and the completely filled d band of Au, result in a novel electronic structure that may account for the catalytic behavior of gold/palladium alloys.[228−237] Fascinating prospects for the design of new catalysts have been opened up using bimetallic particles with layered structures. Schmid et al.[69] have applied the classical seed growth method[238] to synthesize layered bimetallic Au/Pd and Pd/Au colloids with sizes of 20−56 nm. The Au core is coated with Pd by the sequential reduction of gold and palladium salts with sodium citrate. The layered bimetallic colloid is stabilized by trisulfonated triphenylphosphane and sodium sulfanilate. More than 90% of the metal can be recovered in the solid state and redispersion in water is possible in high concentration. Au/Pd and Pd/Au systems on a TiO_2 support have been used in stabilized and non-stabilized forms as heterogeneous catalysts for the hydrogenation of hex-2-yne to (*Z*)-hex-2-ene. Both the palladium-plated gold seeds and the gold-plated palladium particles showed considerably increased activities compared with either pure metal. The lifetimes of the ligand-stabilized colloid catalysts are considerably enhanced by the protecting ligand shell. The influence of the electronegativity difference between Au and Pd on the activity and selectivity of the hydrosilylation reaction[239] on colloidal Pt surfaces[120,121] has been carefully investigated. In essence, the results demonstrate that the activity, selectivity, and lifetime of a metal colloid catalyst may be optimized by a defined variation of the core/shell composition in the bimetallic precursor.

Residues of the stabilizing agents that are still present on the surface of the colloidal metal precursors (1−5 wt-% metal loading on charcoal, glassy carbon, zeolites, TiO_2, Al_2O_3, $CaCO_3$, SiO_2, single-crystal oxides, or HOPG) may act as effective catalyst modifiers, controlling the selectivity and durability of the heterogeneous colloid catalysts (see Figure 13). Ligands such as phosphanes or phenanthrolines,[68] surfactants of various types[7,15] or organic "envelopes" such as polymers[199,240,241] have been found to control the regio- and enantioselectivity of heterogeneous metal colloid catalysts. In the case of the partial hydrogenation of hex-2-yne to (*Z*)-hex-2-ene, Schmid has found that even subtle changes in the chain length of the substituents of the alkyl-substituted phenanthrolines used as colloid stabilizers have a significant effect on the regioselectivity.[242] Seven- and eight-shell palladium clusters on TiO_2, protected by phenanthroline, catalyze the partial hydrogenation of hex-2-yne to (*Z*)-hex-2-ene with a selectivity of 93%. A similar selectivity was achieved using 3-(*n*-decyl)phenanthroline as the stabilizer. On substitution of the phenanthroline with *n*-butyl or *n*-heptyl groups, however, the activity drops dramatically and the subsequent isomerization or total hydrogenation of the (*Z*)-hex-2-ene is completely suppressed. Geometrical, i.e. steric, factors were proposed to explain the strong influence on the selectivity, and indeed this has been illustrated by further examples. A surfactant was found to control the selectivity in the (*Z*)-selective partial hydrogenation of 3-hexyn-1-ol giving leaf alcohol, which is a valuable fragrance [Equation (9)].[243]

(9)

The performance in this reaction, Equation (9), of heterogeneous Pd colloid catalysts on $CaCO_3$,modified by a number of surfactants, was compared with those of conventional Pd/C and Lindlar catalysts under optimized reaction conditions. The selectivity was found to be dependent on both the support and various promoters. The highest activity and best selectivity (98.1%) in formation of the desired (*Z*)-3-hexen-1-ol was found when a lead acetate promoted palladium colloid on $CaCO_3$, modified by the zwitterionic surfactant sulfobetaine-12 (*N*,*N*-dimethyldodecylammoniopropanesulfonate), was employed. Chemisorption measurements showed that residual amounts of the surfactant were still present on the surface of the immobilized particles. This colloid catalyst proved to be twice as active as a conventional Lindlar catalyst and gave 0.5% higher selectivity. Hydrophilic protecting shells allow improved contact between heterogenized metal colloid surfaces and substrates in aqueous media. For example, a hydrophilic ruthenium colloid catalyst on lanthanum oxide was shown to convert benzene into cyclohexene with 59% selectivity at 50% benzene conversion when suspended in an aqueous solution of sodium hydroxide.[244] Chiral molecules on the surface of the metal colloid can induce control of the enantioselectivity. In this context, a new type of enantioselective platinum sol catalyst, stabilized by the alkaloid dihydrocinchonidine, has been designed (see Figure 18).[177,245]

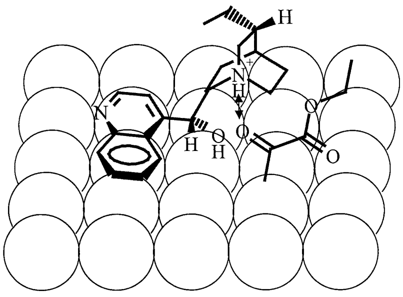
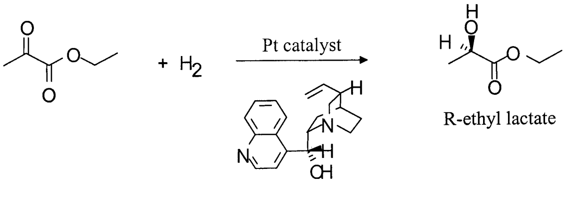


Figure 18. Enantioselective hydrogenation of ethyl pyruvate using dihydrocinchonidine-stabilized Pt colloids (adapted with permission from ref.[15])

The colloidal catalysts were prepared with different particle sizes by reducing platinum tetrachloride with formic acid in the presence of different amounts of the alkaloid. Optical yields of 75−80% *ee* were obtained in the hydrogenation of ethyl pyruvate with chirally modified Pt sols, Equation (10). These catalysts were shown to be structure-insensitive since turnover frequencies (ca. 1 s^{-1}) and enantiomeric excess proved to be independent of the particle size.



(10)

In order to evaluate the catalytic characteristics of colloidal platinum, the efficiency of Pt nanoparticles in the "quasi-homogeneous" reaction shown in Equation (10) was compared with those of supported colloids of the same charge and of a conventional heterogeneous platinum catalyst. The "quasi-homogeneous" colloidal system was found to surpass the conventional catalyst in turnover frequency by a factor of three.[245] Bradley et al.[246,247] and Liu[248,249] have studied the enantioselectivity of the reaction according to Equation (10) in the presence of polyvinylpyrrolidone as a stabilizer. In addition, Bradley[246] has observed that the presence of HCl in such Pt sols, modified by cinchona alkaloids, has a marked effect on the rate and reproducibility. The performance of the catalysts was improved in terms of both reproducibility and rate by the removal of HCl by dialysis. These "purified" colloidal catalysts can be used as reliable test systems in the screening of alternative chiral modifiers to cinchona alkaloids and for precise rate studies. In addition, a systematic variation of the reaction parameters relevant to the catalyst performance is possible without unwanted side effects. It has been shown that an excess of polyvinylpyrrolidone present on a colloidal Pt catalyst is irrelevant to the access of modifier molecules to the colloidal metal surface. However, the polymer may be adsorbed at the metal surface, thereby reducing the number of modified surface sites available for the enantioselective hydrogenation.[247] The stereoselective and enantioselective transformation of specific prochiral substrates into valuable fine chemicals can be achieved through the use of nanostructured metal colloids. The application of rational ligand control based on molecular modeling, which has been successful in homogeneous metal complex catalysis, promises similar results in heterogeneous metal colloid catalysis.

Superior lifetimes can also be expected since it is reasonable to assume, on the basis of the chemisorption results, that the "coating" on catalytically active nanometal particles, which is permeable to small molecules such as H_2 or O_2, effectively prevents contact of the metal surface with poisons. In fact, the lifetimes of the colloid catalysts are considerably longer than those of conventional precipitation catalysts. For example, the activity of a conventional Pd/C catalyst expires completely in the hydrogenation of cyclooctene to cyclooctane after 38,000 catalytic cycles per Pd atom, but the Pd colloid/C catalyst still shows a residual activity after 96,000 catalytic turnovers (Figure 19).[250]

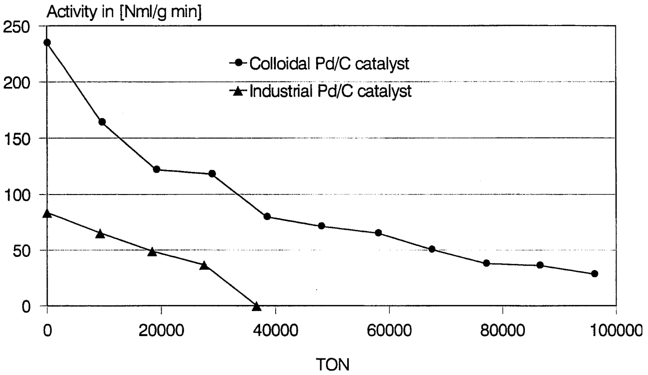
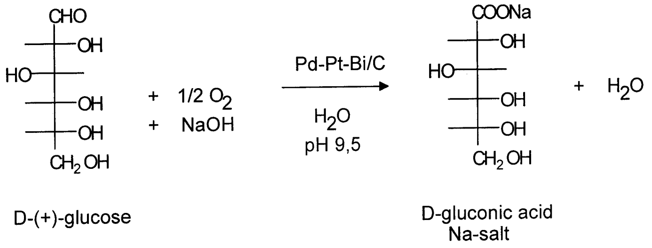
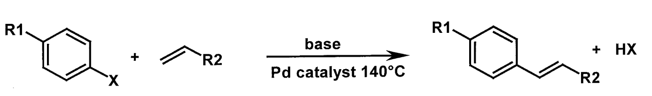


Figure 19. Durability of colloidal Pd/C catalysts in the cyclooctene hydrogenation test compared with a conventional Pd/C system (adapted with permission from ref.[15])

When surfactant-stabilized Pd/Pt precursors were supported on charcoal and promoted by bismuth, superior catalytic oxidation catalysts were obtained.[251] Compared to industrial heterogeneous Pd/Pt catalysts, charcoal-supported $Pd_{88}/Pt_{12}-(oct)_4NCl$ alloy particles (1.5 to 3 nm) were found to offer an excellent activity combined with high selectivity in the oxidation of glucose to gluconic acid by molecular oxygen, see Equation (11).[251] An increased durability of the colloidal Pd/C catalysts was also observed in this case. Much greater retention of the catalytic activity was found for such a system as compared to a conventionally manufactured Pd/C catalyst after recycling both catalysts 25 times under similar conditions. Obviously, the lipophilic $(oct)_4NCl$ surfactant layer prevents the colloid particles from coagulating and being poisoned in the alkaline aqueous reaction medium. Shape-selective hydrocarbon oxidation catalysts have been described, where active Pt colloid particles are present exclusively in the pores of ultramicroscopic tungsten heteropoly compounds.[252] Phosphane-free Suzuki and Heck reactions involving iodo, bromo, or activated chloro substituents were performed using catalytic amounts of ammonium salt or poly(vinylpyrrolidone)-stabilized palladium or palladium nickel colloids [Equation (12)].[145,252]

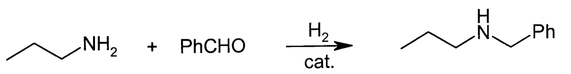


(11)



(12)

The Pd-colloid-catalyzed Heck arylation of styrene with chlorobenzene gave (*E*)-stilbene as the exclusive product. This type of C−C linkage is valuable for the production of pharmaceutical intermediates and fine chemicals. Turnover frequencies (TOF) of more than 80,000 have been achieved in the coupling of *p*-bromobenzaldehyde with butyl acrylate using poly(vinylpyrrolidone)-stabilized palladium as the catalyst.[253] Reetz has applied colloidal, water-soluble PtO_2 (i.e. a colloidal "Adams catalyst") in the immobilized form for the reductive amination of benzaldehyde by *n*-propylamine [Equation (13)].[160,161]



(13)

The selectivity in favor of the desired monobenzylated product was found to be > 99% and the immobilized PtO_2 was found to be four to five times more active than the commercial Adams catalysts. The PtO_2 colloid proved to be effective in the hydrogenation of carbonyl compounds and of olefins, both in solution and in immobilized form. The heterogeneous catalytic amination of aryl bromides by immobilized Pd^0 particles has recently been reported.[252] Secondary amines such as piperidine and diethylamine were used in the amination of aryl bromides. The reactions proceeded with good turnover numbers and regiocontrol. The catalysts could be reused repeatedly without loss of activity or selectivity following filtration from the reaction mixture.

A new class of heterogeneous catalyst has emerged from the incorporation of mono- and bimetallic nanocolloids in the mesopores of MCM-41 or the entrapment of pre-prepared colloidal metals in sol-gel materials.[254−256] Pre-prepared Pd colloids stabilized by phenanthroline obtained by the Schmid method[57−72] have successfully been embedded in MCM-41 mesopores (some colloid is deposited on the external surface) to give CO-oxidation catalysts.[254]

Reetz has developed a strategy for the entrapment of monodisperse nanometal colloids, e.g. R_4NX-stabilized Pd particles.[255] The nanosized particles (2−3.5 nm) are pre-prepared by electrochemical synthesis.[85,90−97] The entrapment in hydrophobic sol-gel materials occurs through the fluoride-catalyzed hydrolysis of mixtures of $CH_3Si(OCH_3)$ and $Mg(OC_2H_5)_2$. Finally, the stabilizer is extracted and the "naked" nanometallic particles are left trapped in the pores (see Figure 20).

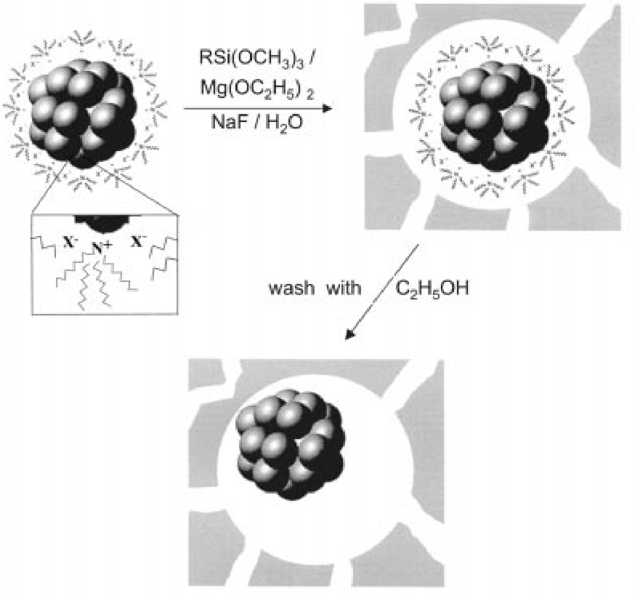


Figure 20. Incorporation of preformed metal colloids in sol−gel materials (adapted with permission from ref.[255])

Ultramicrotomic techniques in combination with shadow-casting TEM have confirmed that the Pd particles are embedded in the oxide matrix and are not fixed on the outer surface. Reetz et al.[255] have also investigated the catalytic properties of the new material. They were able to control the hydrophobicity of the matrix by adjusting the relative amounts of the $CH_3Si(OCH_3)_3$ and $Mg(OC_2H_5)_2$ in the gel. The catalytic activity and selectivity was tested in the partial hydrogenation of COD to give cyclooctene: It was found that the activities of the new systems are governed by the specific pore volume and the hydrophobic properties of the wall. The selectivity for cyclooctene was 93% and the most active of these sol−gel-entrapped Pd catalysts exhibited a considerably higher activity than those of commercially available Pd/Al_2O_3 samples. The preparation of a fully alloyed Pd/Au colloid of 3.0 nm particle size by a modified sol−gel procedure using THF as the solvent and involving the co-reduction of Pd and Au salts with tetraalkylammonium triethylhydroborate,[6] and its subsequent embedding in silica, has been described.[256] The integrity of the incorporated Pd/Au alloy particles remained virtually unaffected. A mesoporous texture with a comparatively narrow pore distribution remained after the removal of the protecting surfactant. According to the physical characterization by a combination of techniques, the SiO_2-embedded Pd/Au colloid retains the size and structural characteristics of the colloidal metal precursor. The material exhibits excellent catalytic properties in selective hydrogenation test reactions. These few examples show that colloidal bimetallic precursors − embedded in matrices or deposited on various supports, and promoted by additives if necessary − may become of practical importance in heterogeneous catalysis.

Fuel Cell Catalysts

"Fuel cell technology" attracts a great deal of interest because it allows the direct conversion of chemical energy into electricity.[257] The catalyst systems are an integral part of the electrochemical reactor utilized in fuel cells. Among the wide-ranging applications of fuel cells are low-emission transport systems, stationary power stations, and combined heat and power sources. Classical studies were carried out in the early 1900s and major innovations and improvements have been achieved over the last few years. The first "new electric cars" are expected to be on the market around 2005, but further developments are still needed, most notably in the area of catalysts. Hydrogen fuel cell catalysts rely on pure Pt, whereas Pt alloy electrocatalysts are employed for the conversion of reformer gas or methanol into electricity. The active component in the latter cases are small Pt-containing bi- or trimetallic particles, 1−3 nm in size, which scatter X-rays as nearly perfect "single crystals". These systems offer improved efficiency and tolerance towards certain contaminants, especially CO, in the anode feed.[258−263] It was clear from patents filed in the early 1970s that finely particulate colloidal platinum sols should be the ideal precursors for the manufacture of fuel cell electrodes.[258]

This section of our microreview focuses on recent developments in catalysts for phosphoric acid fuel cells (PAFCs), proton-exchange membrane fuel cells (PEMFCs), and the aforementioned direct methanol fuel cell (DMFC). The six main types of fuel cell are described in recent reviews.[264−268] PAFCs operating at 160−220 °C use orthophosphoric acid as the electrolyte; the anode catalyst is Pt and the cathode can be, e.g., Pt/Cr/Co.[264−268] For this application, a trimetallic colloidal precursor of the composition $Pt_{50}Co_{30}Cr_{20}$ (size 3.8 nm) was prepared by the co-reduction of the appropriate metal salts.[269−271] The trimetallic particles are alloyed in an ordered *fcc* structure according to XRD analysis. The electrocatalytic performance in a standard half-cell was compared with that of an industrial standard catalyst (trimetallic crystallites of size 5.7 nm) manufactured by co-precipitation and subsequent annealing at 900 °C. The advantage of the trimetallic colloid catalyst lies in its improved durability, which is essential for PAFC applications. After 22 h, it was found that the potential had decayed by less than 10 mV.[272]

PEM fuel cells use a solid proton-conducting polymer as the electrolyte at 50−125 °C. The cathode catalyst is based on Pt alone, but because of the required tolerance to CO a combination of Pt and Ru is preferred for the anode.[258−263] Colloidal Pt/Ru catalysts are currently under widespread investigation for low-temperature (80 °C) polymer membrane fuel cells (PEMFCs).[350,351] They have also been proposed for the use in direct methanol fuel cells (DMFCs) or in PEMFCs, which are fed with CO-contaminated hydrogen produced in on-board methanol reformers. The ultimate dispersion state of the metals is essential for CO-tolerant PEMFCs, and truly alloyed Pt/Ru colloid particles less than 2 nm in size seem to fulfill these requirements.[17,18,20,258,260,273−276] Alternatively, bimetallic Pt/Ru PEM catalysts have been developed for the same purpose, where non-alloyed Pt nanoparticles of < 2 nm and Ru particles of < 1 nm are dispersed on a carbon support.[260] From the results obtained, it can be concluded that a Pt/Ru interface is essential for the CO tolerance of the catalyst, irrespective of whether the precious metals are alloyed. For the manufacture of DMFC catalysts, however, Pt/Ru nano*powders* of size 3−5 nm or thin films are used as the precursors.[261−263] For the electrocatalytic oxidation of methanol, a Pt or a Pt metal alloy catalyst has been developed, where a (phthalocyanine)Ru complex is added as a dopant to significantly enhance the catalytic effect.[271] For comparison, the electrocatalytic activity in the oxidation of CO and a CO/H_2 gas mixture (simulated reformer gas)[17] was compared with that of a bimetallic $Pt_{50}/Ru_{50}-(oct)_4NCl$ colloid prepared by the salt co-reduction method.[6][87−89] The mean particle diameter was 1.7 nm according to high-resolution transmission electron microscopy (HRTEM) [see Figure 21, a)]. The alloyed state of the particles was verified by point-resolved energy dispersive X-ray (EDX) analysis [Figure 21, b)].

Glassy carbon supported $Pt_{50}/Ru_{50}-(oct)_4NCl$ colloids were examined by CO-stripping voltammetry and the data were found to be essentially identical to those found in well-characterized bulk-alloy electrodes. The activity of the colloid in the continuous oxidation of 2% CO in H_2 at a rotating disk electrode was determined at 25 °C in 0.5 M H_2SO_4. The results led to the conclusion that these Pt/Ru colloids

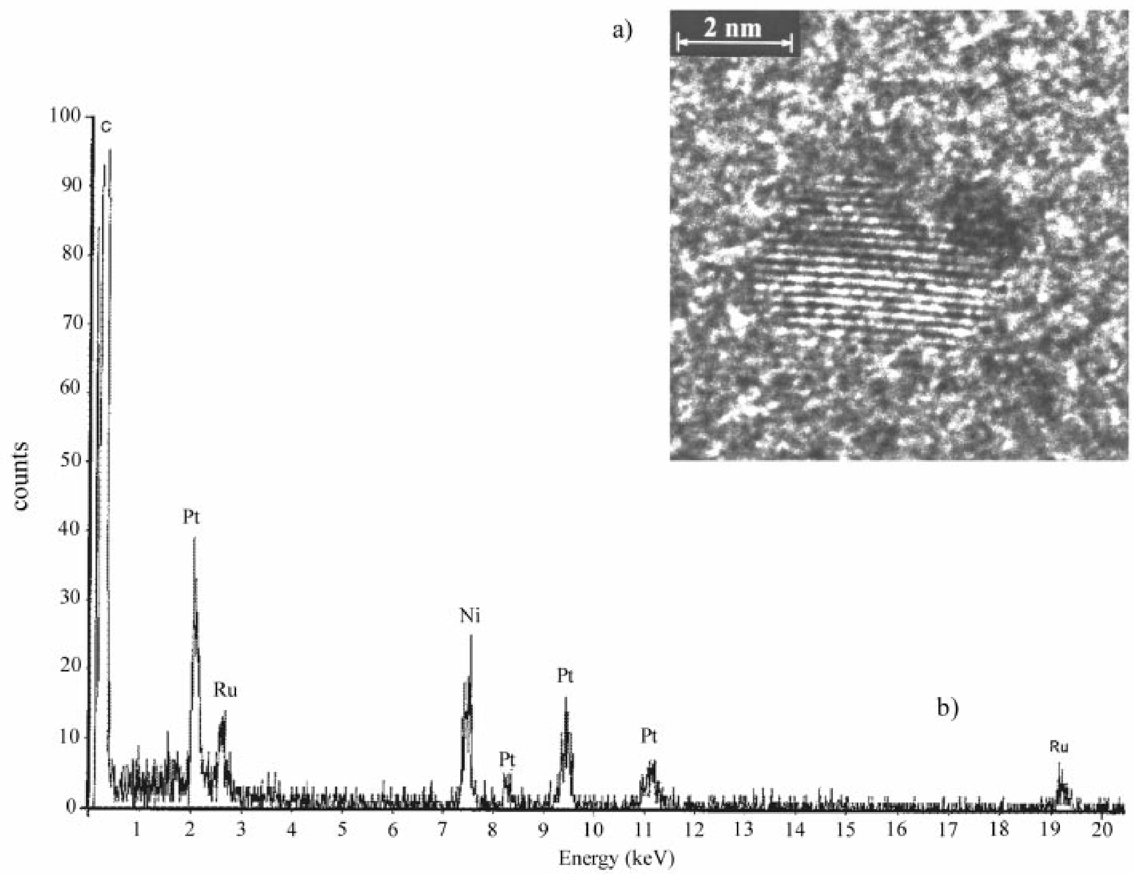


Figure 21. a) High-resolution TEM image of a single $Pt_{50}Ru_{50}$ particle (1.7 nm) (adapted from ref.[17]); b) EDX point analysis (focus 10 nm) of discrete $Pt_{50}Ru_{50}$ particles (adapted with permission from ref.[17])

are very suitable precursors for high-surface-area fuel cell catalysts.[20] XANES data were supportive of the bimetallic character of the particles. In addition, in situ XRD (by Debye function analysis) has revealed the catalytic function of the alloyed Ru in the CO oxidation: Oxide species are formed on the Ru surface at 280 °C, which slowly coalesce to form RuO_2 particles. After re-reduction, the catalyst shows a pure *hcp* ruthenium phase and larger platinum-enriched alloy particles.[277] Scanning probe microscopy (SPM) has been applied in order to characterize the real-space morphology of the electrode surfaces of supported nanostructured metal colloids on the nanometer scale.[278] Colloidal Pt_{50}/Ru_{50} precursors (< 2 nm) raise the tolerance to CO, allowing higher CO concentrations in the H_2 feed of a PEMFC without a significant drop in performance.[18−20] A selective Pt/Mo oxidation catalyst for the oxidation of H_2 in the presence of CO in fuel cells comprises Pt_xMo_y particles, where $x = 0.5-0.9$ and $y = 0.5-0.1$.[279] The colloid method was found to offer a highly suitable exploratory approach to finding improved formulations for binary and ternary anode electrocatalysts. The metals used include Pt, Ru, W, Mo, and Sn.[19] The combinatorial screening method has been successfully applied to electrocatalysts,[280] and it is an obvious step to include colloids in these experiments. As an alternative to the reductive metal colloid synthesis, the so-called "metal oxide concept" was developed, which allows the fabrication of binary and ternary colloidal metal oxides as electrocatalyst precursors [Equation (14)].[160−162]

$$PtCl_4 + RuCl_3 \xrightarrow[\text{stabilizer}]{H_2O/\text{base}} PtRuO_x \text{ colloid} \qquad (14)$$

Colloidal Pt/RuO_x (1.5 ± 0.4 nm) stabilized by a surfactant was prepared by co-hydrolysis of $PtCl_4$ and $RuCl_3$ under basic conditions. By variation of the stoichiometry of the transition metal salts, the Pt/Ru ratio in the colloids could be varied between 1:4 and 4:1. The corresponding zerovalent metal colloids were obtained by the subsequent application of H_2 to the colloidal Pt/Ru oxides (optionally in the immobilized form). Additional metals have been included in the "metal oxide concept" [Equation (14)], so as to prepare binary and ternary mixed metal oxides in colloidal form. $Pt/Ru/WO_x$ is regarded as a good pre-catalyst, especially for application in DMFCs. Main group elements such as Al have been included in multimetallic alloy systems in order to improve the durability of fuel cell catalysts. Alloys of $Pt_3AlC_{0.5}$ with Cr, Mo, or W particles of size $4-7$ nm have been prepared by sequential precipitation on conducting carbon supports such as highly disperse Vulcan

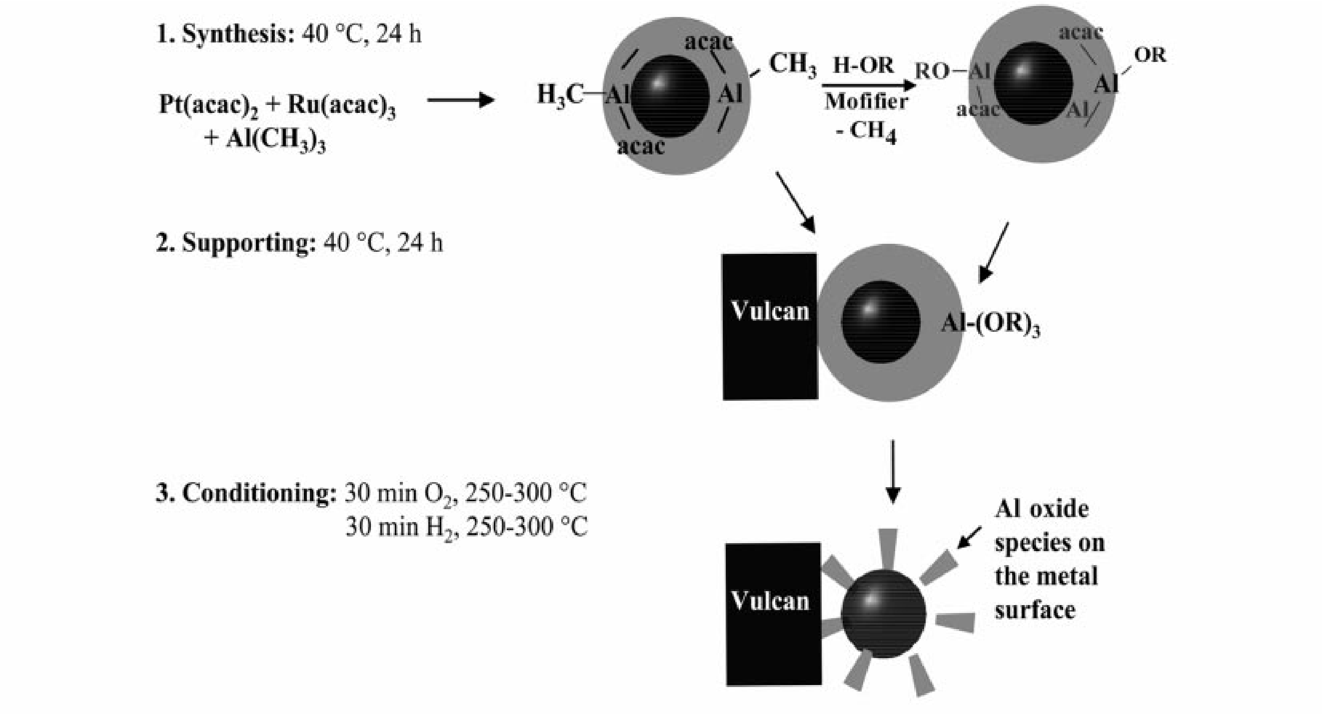


Figure 22. Scheme of the preparation of colloidal Pt/Ru/Al PEMFC anode catalysts (> 20% metal on Vulcan XC72®) by the "precursor concept"(adapted with permission from ref.[273])

XC72®.[281] Alternatively, colloidal precursors composed of Pt/Ru/Al allow the manufacture of multimetallic fuel cell catalysts (1−2 nm) having a metal loading of > 20%. The three-step catalyst preparation is summarized in Figure 22.

The colloidal Pt/Ru/Al precursor is pre-prepared by the organoaluminum route. In the absence of stabilizers, the co-reduction of organic Pt and Ru salts using $Al(CH_3)_3$ gives halogen-free, multimetallic Pt colloids, e.g. $Pt_{50}Ru_{50}/Al$ (size 1.2±0.3 nm). By adjusting the stoichiometric ratio of the metal salts, the ratio of Pt to the second metal in the colloid can be adjusted. The addition of alcohols or suitable surfactants allows the dispersivity of the colloidal precursor in organic media or water to be tailored without affecting the particle size. In the second step, the Pt/Ru/Al colloid is adsorbed on high-surface-area carbon by treatment at 40 °C for 24 h. In the third step (conditioning), the dried Pt/Ru/Al Vulcan catalyst powders are exposed to O_2 and H_2 for 30 min each at 250−300 °C to completely remove the surfactants. The particle size of the Pt/Ru/Al colloid adsorbed on the support was found to be virtually unaffected by the treatment (1.3±0.4 nm) and after the thermal treatment only a moderate growth was evident (1.5±0.4 nm). The aluminum was found to be present on the Pt/Ru surface in an oxidized form. This accounts for the size-stabilization observed in the Pt/Ru particles and for the improved durability of the resulting electrocatalysts. Recently, a fuel cell for generating electric power from a liquid organic fuel ("synfuel") was described. It comprises a solid electrolyte membrane directly supporting the anode and cathode layers, which contain 7−10% Pt and Ru, 70−80% perfluorovinylether sulfonic acid, and 15−20% polytetrafluoroethylene.[276] In conclusion, nanostructured metal colloids are

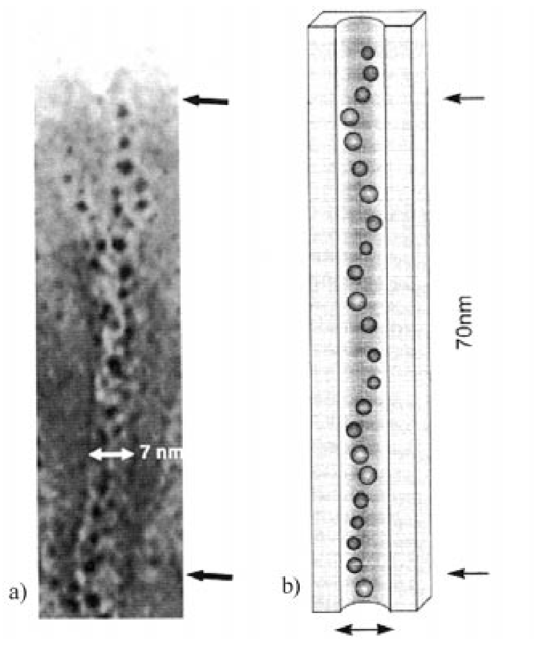


Figure 23. a) TEM image of a one-dimensional Au_{55} cluster wire in a nanoporous alumina membrane; b) schematic representation of the helical wire in a 7 nm pore (adapted with permission from ref.[277])

very promising precursors for manufacturing multimetallic fuel cell catalysts that are truly nanosized (i.e. < 2 nm) and have high metal loadings (20 wt-% of metal).

Potential Applications in Materials Science

It is expected that metal nanoparticles and their assemblies will find numerous applications in materials science. It has been demonstrated that physical properties, including magnetic, optical, melting points, specific heats, and surface reactivity are size-dependent. Quantum size effects are related to the "dimensionality" of a system in the nanometer range. "Zero-dimensional" metal particles might still comprise hundreds of atoms. One-dimensional nanoparticle arrangements (cluster wires) are of potential practical interest as semiconducting nanopaths for applications in nanoelectronics. 1D particle arrangements may be induced through the use of host templates. Using vacuum or electrophoretic methods, Schmid et al.[318−320] were able to fill the parallel channels of nanoporous alumina membranes with chains/rows of 1.4 nm gold particles giving one-dimensional "quantum wires" consisting of insulated 20−100 Au_{55} clusters in a helical array (see Figure 23). The diameter of the nanowire could be controlled by varying the pore size.

Interestingly, 1.4 nm Au particles were found to arrange themselves into a linear row when attached to single-stranded DNA oligonucleotides.[321] Driven by the technological significance associated with such architectures, the fabrication of ordered two-dimensional nanoparticle arrays has been successfully achieved by several research groups, whose work has recently been reviewed.[281][282] Planar arrays of uniform metal nanoparticles would allow the design of new "supercomputers" having a superior data storage capacity. Langmuir−Blodgett films of nanometal systems have frequently been studied in this context. Starting with nanoparticles of defined nuclearity, 2D lattices of thiolized Au_{55}, Pd_{561}, and Pd_{1415} have been prepared.[322] Recently, the first successful preparation of 2D hexagonal and cubic lattices of Au_{55} nanoparticles by self-assembly on polymer films was reported.[163] Simply dipping polyethylenimine-modified surfaces into aqueous solutions of acid-functionalized Au_{55} cluster generates the Au_{55} monolayers shown in Figure 24.

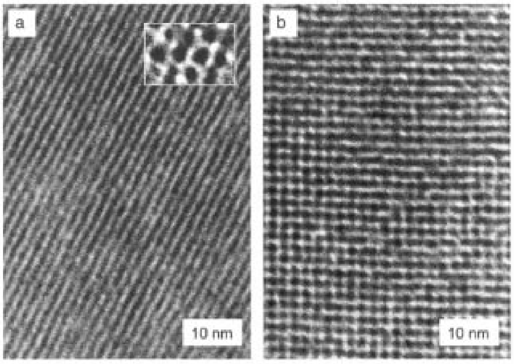


Figure 24. Au_{55} monolayers showing a hexagonal (a) and a cubic (b) structure; the insert in (a) shows single clusters in the hexagonal form (adapted with permission from ref.[163])

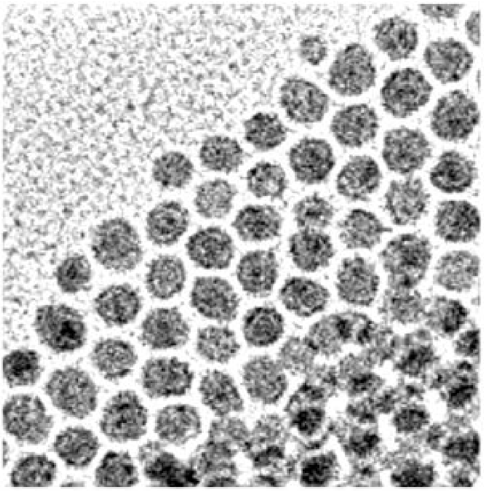


Figure 25. Pd colloid hexagonal close-packed arrangement in the first monolayer (adapted with permission from the Royal Chemical Society from ref.[291])

The interactions between the nanoparticles and the surface are obviously strong enough to prevent mechanical removal. Whereas the hexagonal form shown in Figure 24 (a) is normal for an ordered monolayer, the cubic orientation seen in Figure 24 (b) is unprecedented. Most of the work published on organized nanometal structures has been focused on gold particles and sulfur-containing groups in the various ligands.[283−288] Schiffrin et al. have achieved the self-organization of nanosized gold particles using $R_4N^+X^-$ surfactants.[289] Ramos et al. have recently reported the surfactant-mediated two-dimensional crystallization of colloidal crystals.[290] Making use of the attractive Coulomb interactions between colloids and surfactant structures offers a potential new route to the self-assembly of ordered colloidal structures. Nanostructured palladium clusters stabilized by a monomolecular coating of tetraalkylammonium halide surfactants self-assemble on carbon surfaces in an ordered manner with the formation of *hcp* structures (Figure 25).[291]

The self-organization of magnetic nanosized cobalt particles was studied by Pileni's group.[296,297] A comparison of the magnetic properties of deposited cobalt nanoparticles with those of particles dispersed in a solvent indicated a collective flip of the magnetizations of adjacent particles when they were self-assembled. Pileni et al. have recently published a number of papers concerning the self-assembly of nanoparticles and have developed a number of methods for the manipulation of these systems.[337−339] Mulvaney et al. have described two- and three-dimensional assemblies of metal core/silica shell nanoparticles in a recent review article.[298] A feature article by Balazcs[299] outlines how solid additives can be used to tailor the morphology of bin-

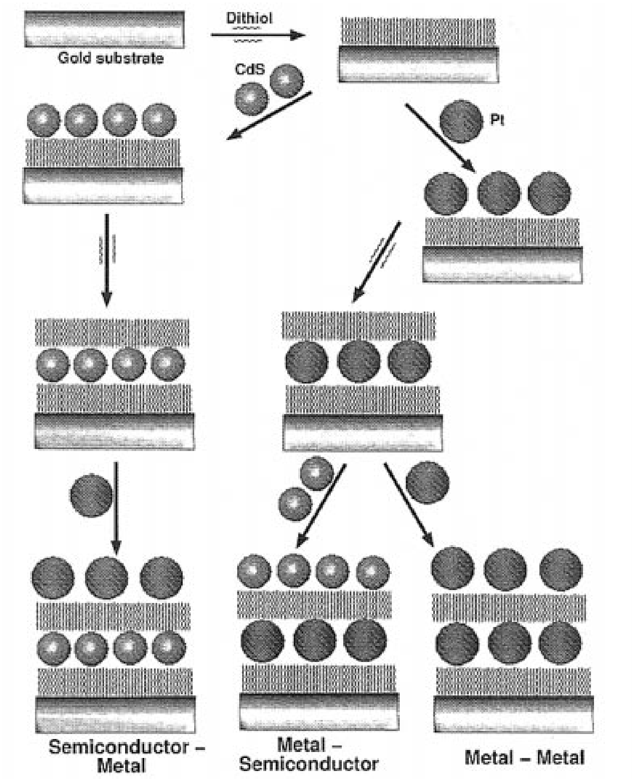


Figure 26. Three-dimensional superlattices obtained by layer-by-layer deposition of Pt particles (or CdS as a semiconductor) onto a dithiol-coated Au substrate (adapted from ref.[165])

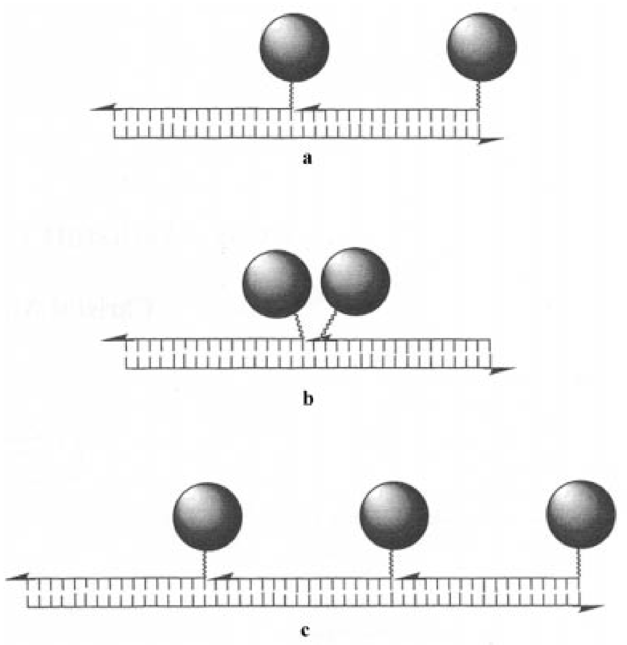


Figure 28. Self-organization of conjugates from gold particles (shaded spheres) and oligonucleotide codons to supramolecular assemblies by the addition of a template strand; derivatization of the oligonucleotides in the 3′- or 5′-position allows control over the mode of head-to-head (a) or head-to-tail (b) homodimers; the trimer (c) is formed using the complementary sequence in triplicate (adapted with permission from ref.[314])

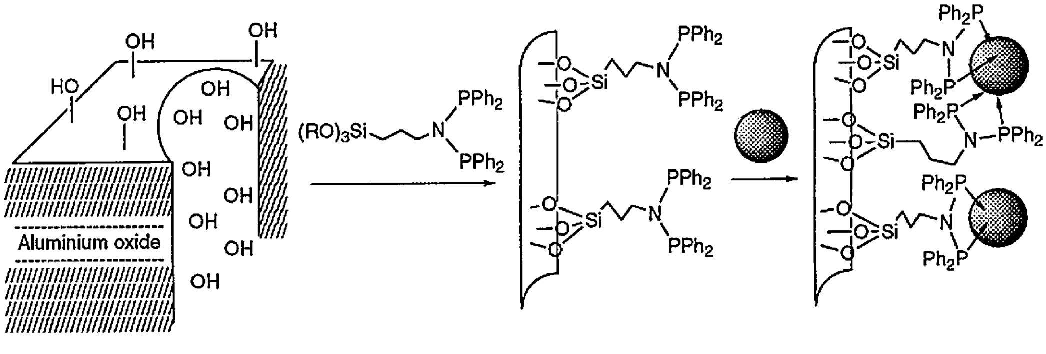


Figure 27. Functionalization of nanoporous alumina membranes and immobilization of metal colloids or clusters on the pore walls (adapted with permission from ref.[349])

ary mixtures containing nanoscopic particles and thereby control the macroscopic properties (e.g., the mechanical integrity) of composites. In addition, computer-aided design has been employed to establish how self-assembled nanostructures can be induced to form arbitrary functional arrays on surfaces.[300] Bifunctional spacer molecules such as diamines have been used in attempts to link nanoparticles three-dimensionally.[301] The multilayer deposition of particle arrays on gold has been successfully achieved by the sequential adsorption of dithiol and near-monodisperse nanometal or CdS particles (see Figure 26).

Several monometal, bimetal, and metal-semiconductor superlattices have been prepared by dipping a gold substrate into the appropriate solutions, with intermediate steps involving washing and drying.[302] The stepwise three-dimensional assembly of layered gold nanoparticles in porous silica matrices has also been reported.[303] Schmid has recently reported strategies for the anchoring of metal complexes, clusters, and colloids within nanoporous alumina (Figure 27).[349]

A different field of technological interest stems from the high spin density of nanostructured magnetic metals of the Fe, Co, Ni series.[304,305] THF-stabilized Mn^0 particles exhibiting superparamagnetism below 20 K were described as the first example of an antiferromagnetic metal colloid.[306]

New strategies utilizing DNA as a construction material for the generation of biometallic nanostructures have made it possible to develop larger "nanotechnology devices" (< 100 nm) for microelectronic photolithographic applications. DNA is regarded as a promising construction material for the selective positioning of molecular devices because of its recognition capabilities, physicochemical stability, and mechanical rigidity. Seeman was the first to propose DNA for the precise spatial arrangement of 3D networks.[307,308] Assemblies of DNA-derivatized gold colloids have recently been prepared by the DNA hybridization-based self-organization pathway and the resulting defined arrangements of nanometal particles have found applications in electronic, optical, and laser technologies.[309−313,340−345] For example, Alivisatos et al.[310] have obtained defined mono adducts from commercially available 1.4 nm gold clusters where one reactive maleimido group was attached to every particle. These were coupled with thiolated 18-mer oligonucleotides in order to add an individual "codon" sequence. When a single-stranded DNA template containing complementary codons was added, the self-assembly of nanocrystal molecules was observed (Figure 28).[310,314] This work has been the subject of recent reviews.[314−316]

Niemeyer[315] has recently reported the coupling of metal particles bearing a biotin substituent with the DNA−streptavidin hybrid. The growth of a 12 µm long, 100 nm wide conductive silver wire was achieved using a DNA molecule stretched between two gold electrodes as a template.[317] It remains to be seen how the practical applications of these materials will develop over the next few years.

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