

Ligand-stabilized metal clusters and colloids: properties and applications †

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In this perspective some general phenomena of ligand-stabilized transition-metal clusters and colloids are introduced before some recent results on the special behaviour of such particles in catalysis are given.

Continuous reduction of the size of a solid material must finally result in a situation where the typical properties of the material begin to disappear. A few hundred or even thousand sp^3 -hybridized carbon atoms will probably not behave like diamond, and, as is well known since the discovery of the fullerenes, 60 or 70 sp^2 -hybridized carbon atoms do not exist as small graphite-like particles but instead form spherical 'bucky-balls'. Besides possible structural effects, one of the most striking features of particles in the nanometer range will become visible in quantum size effects including any number of novel properties. Quantum size effects are related to the dimensionality of a system. A three-dimensional system is an object with an infinite extent in all three directions. The dimensionality two, realized in layered systems such as atomic monolayers, but also thin films, is characterized by a limited number of layers. Consequently, a one-dimensional material is represented by wires on an atomic or molecular scale and is realized in fibres or polymers. Finally, a zero-dimensional system is a particle which is reduced in all directions to such an extent that the properties of the original bulk system cannot be maintained and so dramatic changes of physical properties are implied.¹ Applying this knowledge to metallic systems, the well known properties of bulk metals can also be expected to change if the size of a metal particle is sufficiently reduced in one, two or even three dimensions. Zero-dimensional metal particles may still consist of thousands or at least hundreds of atoms. The decisive difference compared with a three-dimensionally oriented material is the loss of its characteristics, such as magnetic domain size, scattering length of conduction electrons and the De Broglie wavelength of the electron, and even changes in melting points can be considered as being caused by size reduction.

Metal particles having zero-dimensional properties are found in the world of clusters and colloids. The term 'cluster' is often used for particles smaller than *ca.* 10 nm; larger particles are usually called 'colloids'. Indeed, this very rough borderline separates molecular species from those showing typical colloidal behaviour such as the Tyndall effect. A definition of higher precision and practical value may involve the description of clusters as particles consisting of a more or less distinct number of structurally defined atoms. On the contrary, colloids show broader particle size distributions and predominantly do not possess monocrystalline character. In the following, this latter description of clusters and colloids will be used to decide between both. However, it must be stated that there exist situations where such a distinction cannot be made and both characterizations can be used.

To study the physical properties of clusters and colloids and also, as will be shown below, to apply them in catalysis, it is necessary or at least advantageous to cover them by a

protecting shell of ligand molecules. Protection by small metal particles is, in any case, a condition to make them isolable. Furthermore, ligand-protected clusters and colloids become soluble in various solvents, depending on the nature of the ligands. The most important effect, however, is the prevention of coalescence processes which would take place immediately after contact between 'naked' clusters or colloids.

During the last decade a series of large ligand-stabilized transition-metal clusters and colloids has been prepared, characterized and investigated.² Those in the size range of 1–2 nm show a behaviour which can indeed be correlated with quantum size effects and so follow impressively the predictions discussed above. Some of the properties promise future applications in nanoelectronics.³ The ordered arrangement of 1.4 nm gold clusters in a monolayer has recently been reported.⁴ For such two- or even one-dimensional cluster arrangements, separating the clusters from each other by a chemically variable ligand shell is one of the conditions for their use as quantum dots in nanoelectronics.

What have quantum properties to do with catalytic behaviour? A lot! Numerous papers in the past have reported on the relation between particle size and catalytic activity and selectivity, respectively. As a reason why particle size influences catalytic properties it is argued that changes in geometry, *e.g.* the number of edges, corners, faces, *etc.*, are responsible. Without doubt, this is true. However, from our knowledge about the influence of the particle size on the electronic properties we must conclude that the catalytic properties of a metal cluster are considerably determined by quantum size effects. This can easily be understood: a metal atom on the surface of a particle which is fully metallic differs significantly from an atom in an equivalent position, but as part of a small cluster which has lost its metallic nature. The complete loss of the metallic state means nothing but the absence of freely mobile electrons! The interest in the study of the catalytic properties of ligand-protected colloids and clusters results partially from these considerations. However, there is another advantage in the use of ligated metal particles as catalysts: the ligands influence activity and selectivity as they do in catalytically active complexes. So, with the particles size and shape and the tailoring of the ligand molecules, we have two tools to improve catalytic processes. The results which are reported in this Perspective are exclusively achieved by the use of immobilized or solid colloids and clusters. Former efforts to use them as homogeneous working catalysts in solution more or less failed as decomposition always accompanied the reactions. On the other hand, a special reaction has been described recently where clusters in solution worked as catalysts without recognizable decomposition.⁵

Preparation and Characterization of Ligand-stabilized Colloids and Clusters

The reduction of metal salts in solution is the method most often used to generate colloids. Especially colloids of noble

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Non-SI unit employed: atm = 101 325 Pa.

metals can easily be prepared in aqueous solution, but also in other solvents. The size of the particles depends on the reducing agent and the conditions such as concentration and temperature. Colloids in water are at least temporarily stabilized by ions present in the solution. The well known red gold sols, which were described by Faraday in the last century, are stable over months and even years. Polar organic solvents can also be used for the generation of colloidal systems, and in some cases the solvent and the reducing agent are identical. However, colloids which are stabilized by simple ions or solvent molecules cannot be isolated as solid material. This is, on the other hand, a condition for the physical and chemical properties to be investigated intensively. For that reason we developed a simple method to protect colloidal particles with a skin of ligand molecules which are co-ordinated by strong chemical bonds and which are not removed when the materials are isolated and completely dried.⁶ Stable gold colloids in the size range of *ca.* 15–35 nm become available if H₂AuCl₄ is reduced by trisodium citrate and the blood-red dilute aqueous systems are treated with an excess of PPh₂(C₆H₄SO₃Na-*m*) or better P(C₆H₄SO₃Na-*m*)₃. These triphenylphosphine derivatives not only substitute weakly bonded ions and solvent molecules to give stable Au–P bonds, but in addition they stabilize the gold colloids by the ionic moieties. The function of the SO₃Na groups becomes obvious when the trisulfonated derivative is used instead of the monosubstituted one. The stability of the colloids in solution increases considerably. Solid phosphine-protected gold colloids can be gained by concentration of the dilute solutions and addition of *e.g.* ethanol. The metallic-looking solids can be redispersed in any concentration. Palladium and platinum colloids can be prepared by analogous procedures. Here, *p*-H₂NC₆H₄SO₃Na turned out to be a suitable ligand.

Recently we succeeded in generating the first ligand-stabilized nickel colloids. They are formed from nickel(II) acetylacetonate and AlEt₂H as a reducing agent in the presence of PPh₃.⁷ As it turned out, the 4 nm colloids are mostly covered by PPh moieties and not by PPh₃ itself. Various attempts to generate rhodium colloids have been described.⁸ Only the method of Bönemann *et al.* using LiBEt₃H led to species of interest with respect to our goal, to prepare stabilized colloids with an at least roughly defined ligand shell. The first isolable rhodium colloids with a phosphine ligand shell were recently generated by us.⁹ If [Rh(H₂O)₆]³⁺ in aqueous solution is treated simultaneously by trisodium citrate and 30 atm H₂ at 60 °C, dark brown sols of rhodium colloids are formed. Addition of an excess of P(C₆H₄SO₃Na-*m*)₃ stabilizes the colloids in such a manner that they can be precipitated by ethanol from the aqueous solution as a dark brown powder which can be redispersed in water. The size of the colloids has been determined by TEM (transmission electron microscopy). Two dominant particle sizes could be detected, depending on the concentration of the starting [Rh(H₂O)₆]³⁺ solution. A 4.4 × 10⁻⁴ mol dm⁻³ solution gives 3.8 ± 0.7 (standard deviation) nm colloids; a solution containing only 20% of that rhodium concentration gives 2.0 ± 0.4 nm particles (Fig. 1). The synthesis has to be carried out in an atmosphere of N₂. Working in air, the phosphine is oxidized to P(C₆H₄SO₃Na-*m*)₃O which is not such a good ligand. Consequently, once isolated the colloids can only partially be redissolved. From elemental analyses one can conclude that a minimum of *ca.* nine phosphine molecules is necessary for a successful redispersion and *ca.* 50 ligand molecules to protect the 3.8 nm colloids sufficiently.

Clusters of that size range are realized in the case of palladium.¹⁰ Palladium(II) acetate can be reduced in acetic acid solution by 1 atm hydrogen at room temperature and in the presence of appropriate ligands. The successfully used ligand molecules are given in Scheme 1. The reactions result in the formation of seven- (7Pd) and/or eight-shell (8Pd) clusters

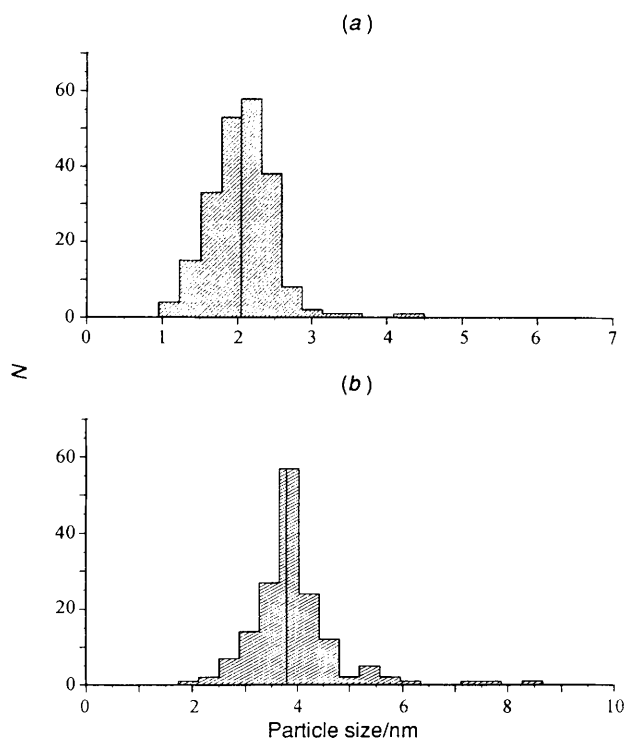


Fig. 1 Particle size distributions of two rhodium colloids, (a) 2.0 ± 0.4, (b) 3.8 ± 0.7 (standard deviation) nm, formed from aqueous [Rh(H₂O)₆]³⁺ solutions of different concentrations by simultaneous reactions with H₂ and trisodium citrate at 30 °C

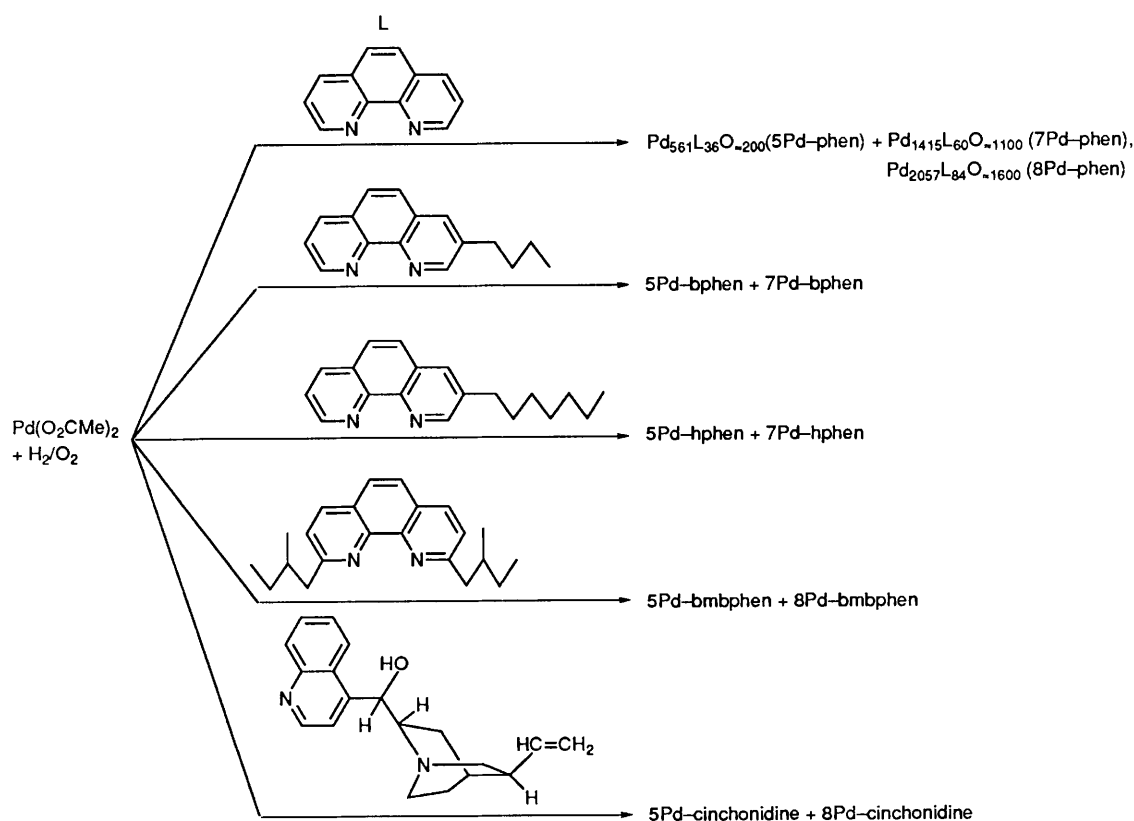
and, in any case, a fraction of five-shell clusters (5Pd). A TEM image of a single 8Pd cluster is shown in Fig. 2.¹⁰ Fig. 3 shows a layer of 5Pd clusters of idealized formula Pd₅₆₁(phen)₃₆O_{≈200}* revealed by scanning tunnelling microscopy (STM).¹¹ The clusters form the top layer of a cluster pellet which was used for conductivity measurements.

Fig. 4 shows an STM image of Pt₃₀₉L₃₆O₃₀ cluster [L = disodium 1,10-phenanthroline-4,7-bis(benzene-4-sulfonate)] molecules as a thin layer on glassy carbon.¹¹ A TEM image of a naked Pt₃₀₉ cluster is shown Fig. 5.¹² The Pt₃₀₉ four-shell clusters are prepared in an analogous reaction to that of the palladium clusters, namely from platinum(II) acetate in acetic acid with gaseous hydrogen in the presence of ligand L.

Two-shell 1.4 nm clusters, especially those of the element gold, are available using phosphine stabilization, starting with [Au(PR₃)Cl] complexes which can be reduced by B₂H₆.¹³ From an electronic point of view these clusters represent particles with the 'last metallic electrons'. They symbolize the interesting transition from the metallic to the semiconducting state, characterized by a definite electronic energy-level splitting.¹⁴ Single Au₅₅(PPh₃)₁₂Cl₆ clusters can be seen in Fig. 6, where the surface of a pellet from an STM experiment is shown.¹⁴

Some of the colloids and clusters described above have been successfully used on supports and in the solid state in heterogeneous catalysis. A few representative results are described below.

* Formulae showing such an accurate stoichiometry have to be considered as idealized. Even when HRTEM and other methods indicate a distinct full-shell structure and analytical data enable the description of the ligand shell, deviations from the ideal composition occur, especially where the clusters consist of a thousand or more metal atoms. In spite of this lack of accuracy we use the term 'cluster' and not 'colloid' to represent the almost perfect monodisperse character.



Scheme 1 Synthesis of five-, seven- and eight-shell palladium clusters using various ligands L

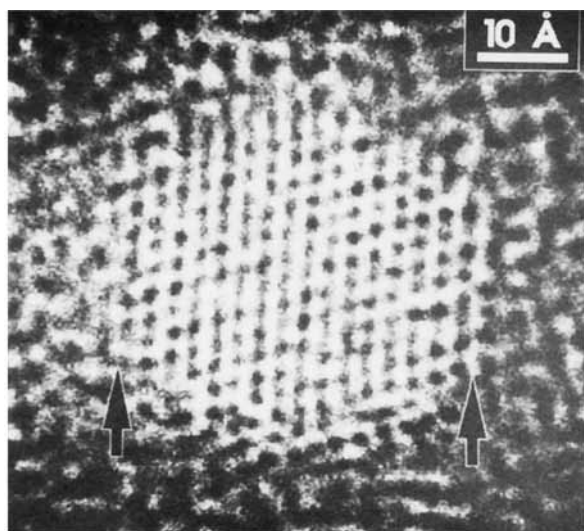


Fig. 2 High-resolution transmission electron microscopy (HRTEM) image of an eight-shell palladium cluster, consisting of 17 face-centred-cubic (f.c.c.)-packed atomic rows. The ligands cannot be imaged

Catalysis with Immobilized Clusters and Colloids

Immobilization of ligand-protected clusters and colloids seems to be a condition for these materials to be applied in catalysis. A few exceptions, where clusters have been used repeatedly in solution,⁵ do not really change the situation. Catalytic success has also been reported using colloids dispersed in polymers,² however realistically such systems cannot be considered as classical solutions. Here, we shall focus exclusively on the use of ligand-protected particles on supports or in some cases in the pure solid state as we found

that the stability can be guaranteed in a wide range only under heterogeneous conditions.

The absorption of clusters and colloids normally occurs very easily by contact of the solid support material with solutions of the clusters or colloids. As supports, zeolites, TiO_2 , Al_2O_3 , CaCO_3 , SiO_2 or active carbon can be used depending on the particular system. The amount of clusters and colloids on the support varies between 1 and 5 wt%.

A series of mixtures of five-, seven- and eight-shell clusters is shown in Scheme 1. All of them can in principle be used as hydrogenation catalysts. As the 7Pd and/or the 8Pd fractions in all cases are formed with 80–90% yield, they have been selected to serve as heterogeneous catalysts in hydrogenation reactions. As an example, the semihydrogenation of hex-2-yne will be discussed here, as it is a very useful reaction to test the activity and selectivity of a hydrogenation catalyst.

A mixture of seven- and eight-shell palladium clusters, protected by phenanthroline and O_2 (7/8Pd-phen) on TiO_2 catalyses the semihydrogenation of hex-2-yne to *cis*-hex-2-ene very selectively, if the alkyne is dissolved in *n*-octane and treated with gaseous hydrogen at room temperature under normal pressure. A maximum of ca. 93% *cis*-hex-2-ene is formed after about 75 min, corresponding to a turnover frequency (TOF) of 35 min^{-1} [Fig. 7(a)]. A similar result is obtained if the phenanthroline molecules are substituted by an *n*-decyl group at the 3 position (7/8Pd-dphen) [Fig. 7(b)]. The activity is reduced, and the maximum of *cis*-hex-2-ene formation is reached after ca. 200 min. The completely different ligand molecule (–)-cinchonidine in 8Pd-cinchonidine again causes *cis*-hex-2-ene formation with a maximum after ca. 150 min [Fig. 7(c)]. On the contrary, substitution of phenanthroline by *n*-butyl (7Pd-bphen) or *n*-heptyl (7Pd-hphen) groups changes the activity and selectivity dramatically. The TOF value drops to 3 min^{-1} . However, as can be seen from Fig. 7(d), there is almost no consecutive reaction over ca. 3000 min indicating that the *n*-butyl and *n*-heptyl derivatives exhibit very little activity towards isomerization or further hydrogenation of *cis*-hex-2-ene. This

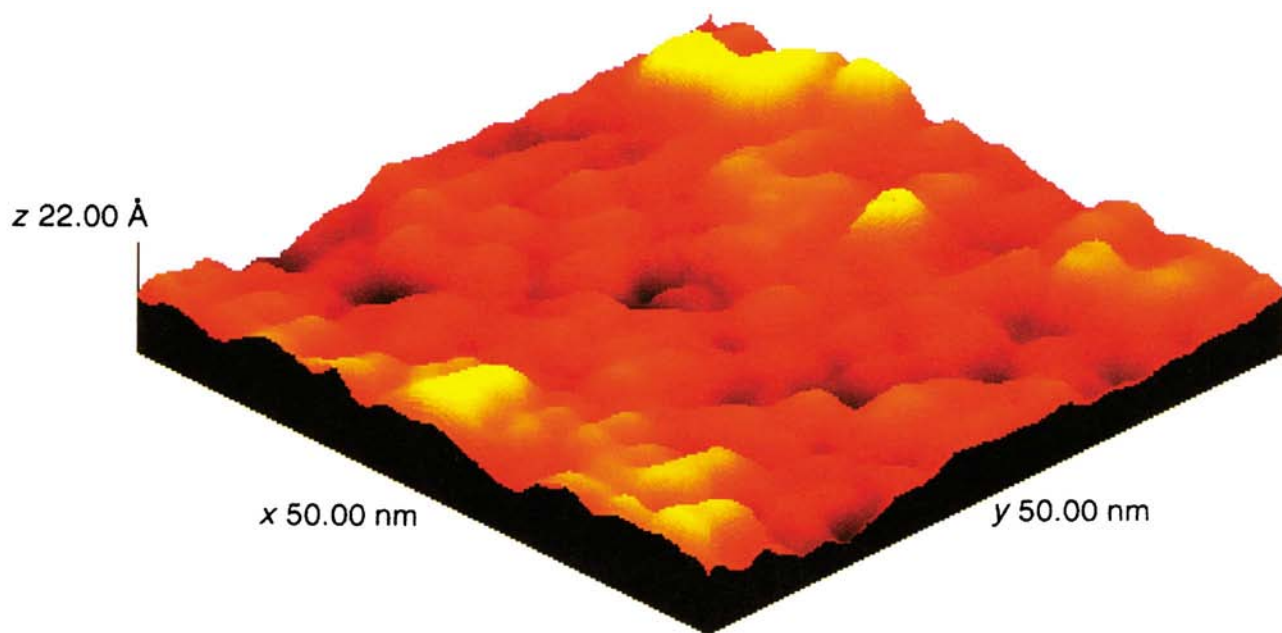


Fig. 3 Scanning tunnelling microscopic image of the surface of a $\text{Pd}_{361}(\text{phen})_{36}\text{O}_{200}$ cluster pellet, showing the cluster together with the ligand shell

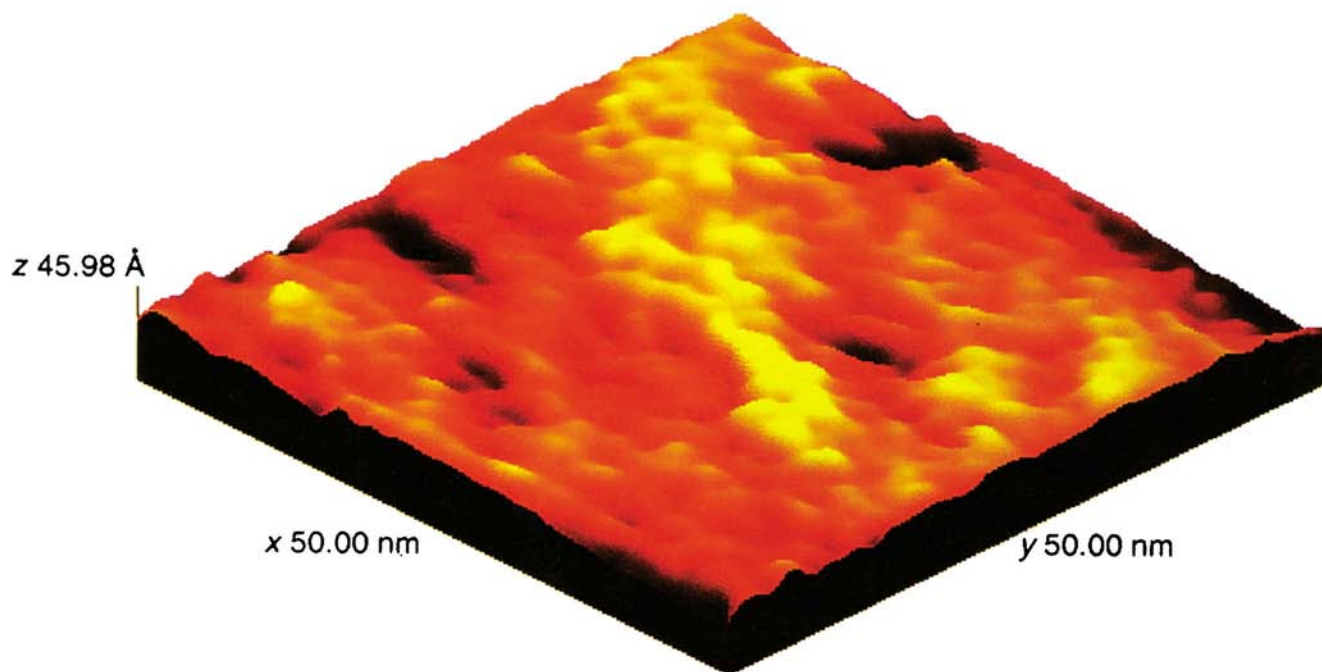


Fig. 4 An STM image of a thin layer of $\text{Pt}_{309}\text{L}_{36}\text{O}_{30}$ clusters on glassy carbon (see text for definition of L)

behaviour cannot be explained without a computer modelling of the situation on the cluster surface which we are just beginning to do. Obviously geometrical reasons are responsible for the unexpected findings as electronic arguments fail to explain the difference, *e.g.* between a *n*-heptyl and a *n*-decyl group.

The influence of ligand geometry in hydrogenation reactions can be demonstrated by further examples. The 2,9-bis(2-methylbutyl)-1,10-phenanthroline-protected eight-shell palladium cluster (8Pd-bmbphen) on active carbon in ethanol hydrogenates acetophenone to phenylethanol with a TOF of 45.5 h^{-1} [Fig. 8(a)]. (–)-Cinchonidine, used instead of the phenanthroline derivative, deactivates the cluster completely with respect to this reaction [Fig. 8(b)]. Even an increase of temperature up to $60 \text{ }^\circ\text{C}$ and of dihydrogen pressure up to 100 atm does not change the situation. (–)-Cinchonidine on 8Pd , on the other hand, was shown to be quite active with respect to hex-2-yne semihydrogenation (see above).

These results demonstrate impressively how relatively small

changes in the ligand geometry result in a remarkably different catalytic behaviour, especially with respect to the selectivity, and make ligand-stabilized clusters interesting future objects in catalysis.

The rhodium colloids, described above, have also been tested as hydrogenation catalysts, as Rh is known to act in various catalyses very successfully. A commercially available rhodium catalyst on active carbon (Rh/C) was used for comparison to see the advantage or disadvantage of the ligand-stabilized colloids. The reaction conditions correspond to those used with the palladium catalyses. Fig. 9 shows the hydrogenation of hex-1-ene using 2 nm colloids on active carbon. A part of the olefin isomerizes to give *cis*- and *trans*-hex-2-ene. However, after 160 min all the hex-1-ene is converted into *n*-hexane. The reaction using the 3.8 nm rhodium colloids on active carbon is similar, however the activity is decreased as can be seen from Fig. 9(b), where the activities of both catalysts are compared with that of the commercial Rh/C catalyst. The isomerizations, observed in

both cases, can be discussed in terms of the Horiuti and Polanyi associative mechanism, including σ/π rearrangements of the adsorbed intermediates.¹⁵ As can be seen, the 3.8 nm rhodium catalyst is of similar activity to the commercial system, whereas the 2 nm colloids show a characteristically increased activity with TOF = 20 min⁻¹.

Hirai and co-workers^{8,16} also compared polymer-stabilized rhodium colloids with industrially applied Rh/C catalysts. Though the catalytic conditions employed for rhodium colloids in polymers are not comparable with ours, a relative comparison is enabled using the industrial material.¹⁶ Interestingly, variations of the rhodium particle diameters from 0.9 to 4.0 nm did not result in significant differences in hydrogenation of hex-1-ene. However, the rhodium colloids in poly(vinylpyrrolidone) and poly(vinyl alcohol), respectively, hydrogenate hex-1-ene four to five times faster than does the industrial Rh/C catalyst, whereas our 2 nm Rh on carbon is only about twice as good as the latter.

The selectivity of the novel rhodium colloids has been tested by means of the semihydrogenation of hex-2-yne, as was done with palladium clusters. As can be seen from Fig. 10, the maximum of *cis*-hex-2-ene formation using the 3.8 nm colloid is accompanied by considerable amounts of *n*-hexane and some *trans*-hex-2-ene. After ca. 500 min *n*-hexane formation reaches 100%. The 2 nm colloids behave very similarly. The rate of *n*-hexane formation increases rapidly after the complete consumption of hex-2-yne as the active surface sites are now

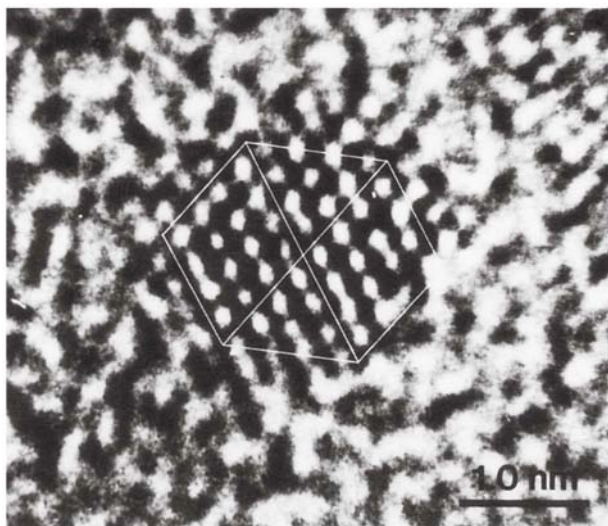


Fig. 5 A TEM image of a single Pt₃₀₉ cluster. Nine rows of f.c.c.-packed Pt atoms characterize it as a four-shell cluster

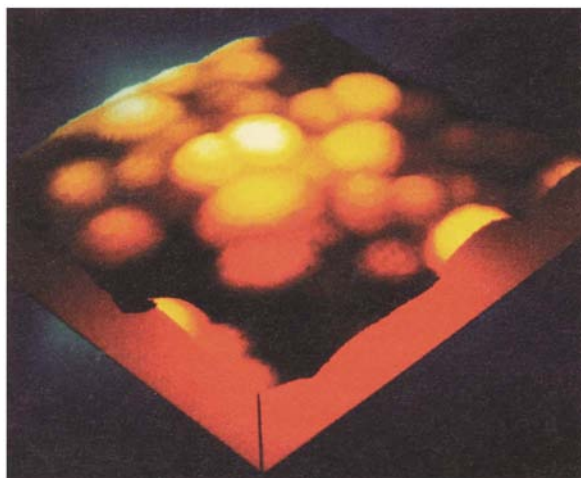


Fig. 6 An STM image of single Au₅₅(PPh₃)₁₂Cl₆ clusters on the surface of a cluster pellet

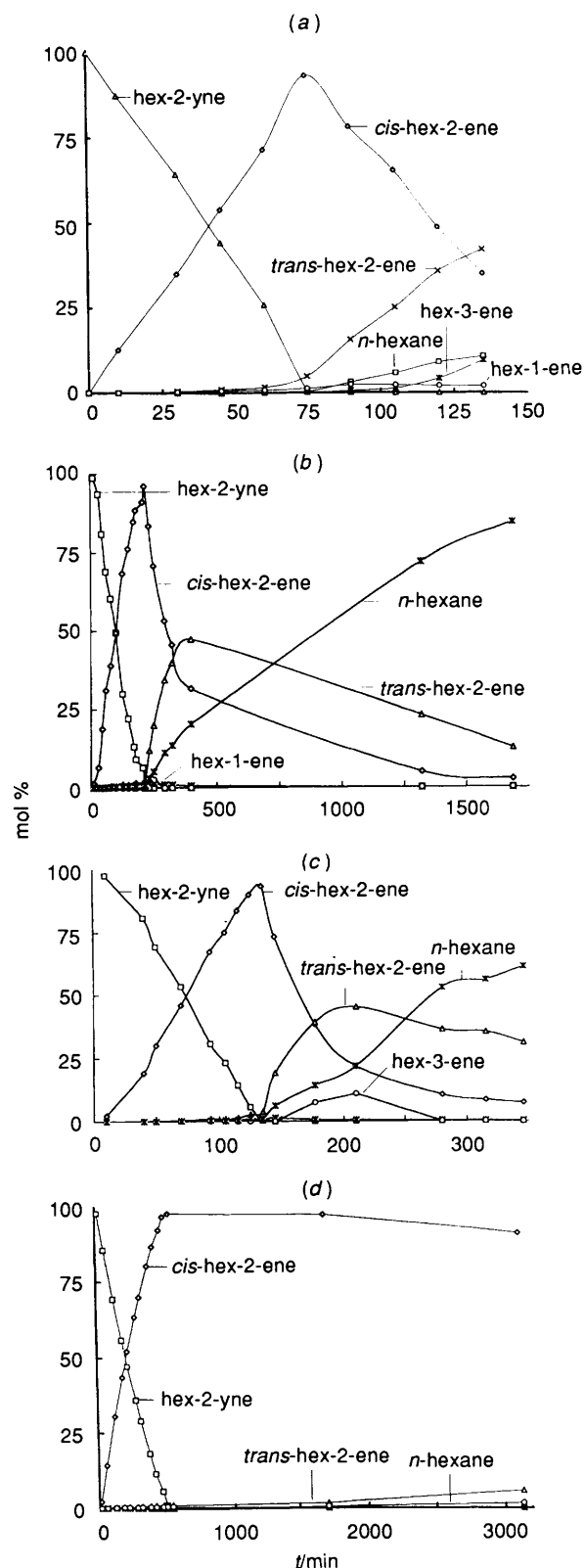


Fig. 7 Hydrogenation of hex-2-yne by 7/8Pd clusters with different ligand shells. In 7(a) the course of reaction with 1 wt% 7/8Pd-phen on TiO₂ (active carbon as support gives very similar results) is shown. After formation of ca. 95% of *cis*-hex-2-ene, consecutive products, mainly *trans*-hex-2-ene, are formed. Substitution of the phen ligand by a *n*-decyl group at the 3 position (1 wt% 7/8 Pd-dphen on active carbon) decreases the activity. The maximum of *cis*-hex-2-ene formation is reached after ca. 200 min, followed by the formation of *trans*-hex-2-ene and *n*-hexane (b). Use of the completely different ligand molecule (—) cinchonidine (1 wt% 8 Pd-cinchonidine on active carbon) results in a similar course of reaction (c). The relatively insignificant substitution of phenanthroline by *n*-butyl (1 wt% 7 Pd-bphen on active carbon) results in an almost exclusive selectivity with respect to *cis*-hex-2-ene formation (d)

obviously available exclusively for hexene hydrogenation. The selectivity agrees well with that of the commercial Rh/C catalyst.

Comparison of the catalytic properties of the ligand-stabilized palladium clusters and of the rhodium colloids with respect to hydrogenation of alkenes and alkynes favours the former. Especially the selectivity for hex-2-yne semihydrogenation by the palladium clusters surpasses that of the rhodium colloids.

A last but very informative investigation, concerning the catalytic behaviour of *bimetallic* colloids, has recently been finished.¹⁷ The so-called germ-growth method enables the easy generation of bimetallic colloids.¹⁸ Germs of *e.g.* gold are prepared as usual. In a second reaction step another metal, here we use Pd, grows on the gold colloids if PdCl₂ is reduced by [H₃NOH]Cl. The thickness of the palladium shell on the gold nuclei depends on the concentration of the palladium salt.

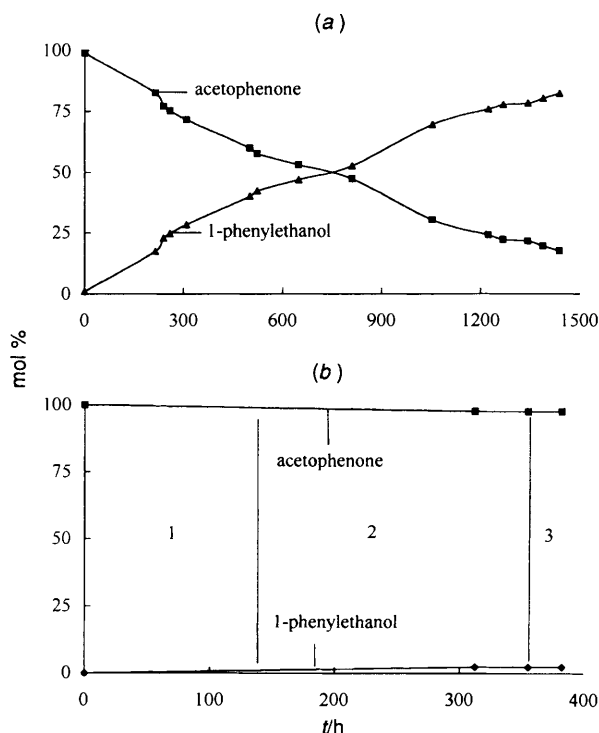


Fig. 8 Hydrogenation of acetophenone to phenylethanol using (a) 8 Pd-bmbphen (1 wt% on active carbon). (—) Cinchonidine on the same 8Pd cluster (1 wt% 8Pd-cinchonidine on active carbon) inhibits the hydrogenation completely (b), even under 100 atm H₂ and at 60 °C. Regions: 1, room temperature, 1 atm H₂; 2, 60 °C, 1 atm H₂; 3, 60 °C, 100 atm H₂

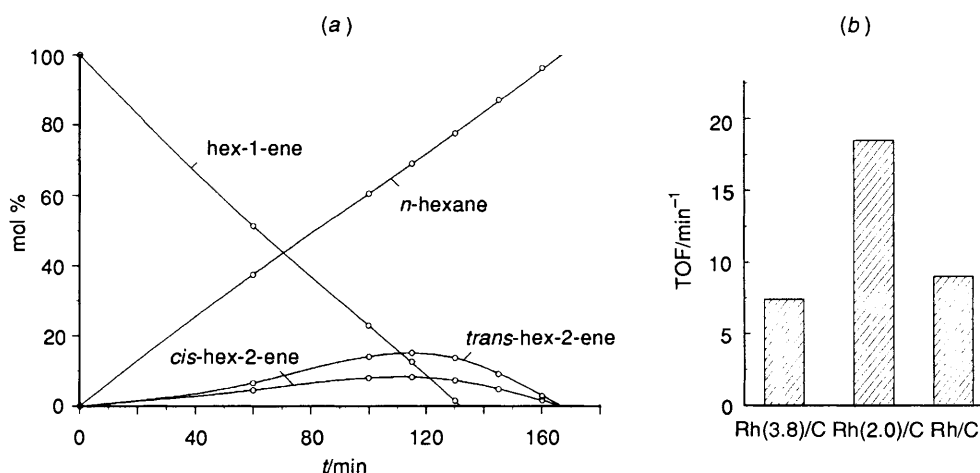


Fig. 9 Hydrogenation of hex-1-ene by rhodium colloids on active carbon: (a) the course of reaction using 2 nm rhodium colloids (0.6 wt%), stabilized by trisulfonated triphenylphosphine on active carbon as support; (b) the TOF values of the hex-1-ene hydrogenation by 2 nm (0.6 wt%) and 3.8 nm colloids (1–1.5 wt%) and for comparison by the commercially available Rh/C catalyst (5 wt%)

After formation of the bimetallic particles they are stabilized by *p*-H₂NC₆H₄SO₃Na. The colloids were isolated as for the monometallic species.

Gold–palladium colloids with a very thin palladium skin (1–2 atomic layers) have been found to be very active catalysts in the solid, but unsupported state for acetylene cyclization at room temperature. This catalyst has been studied by X-ray powder diffraction and *in situ* extended X-ray absorption fine structure during warming to an annealing temperature of 873 K. A preannealing temperature range between 300 and 573 K was found where the particle size distribution remains constant; intermixing of Au and Pd, however, occurs. Only temperatures up to 873 K give larger alloy-like particles. Interestingly, the catalytic behaviour of the colloids changes characteristically when preannealing starts. Fig. 11(a) shows the formation of products from acetylene as a function of temperature. The main product is benzene, accompanied by *n*-hexane, isobutene and some *cis*- and *trans*-but-2-ene. The maximum of benzene formation is observed at *ca.* 500 K. At temperatures above \approx 500 K, synonymous with particle growth, the selectivity towards *n*-hexane and isobutene formation increases. Fig. 11(b) shows the selectivity of the Au/Pd colloids towards C₆ product formation. As can be seen, benzene formation dominates *n*-hexane formation with increasing Au–Pd intermixing.

Outlook

Ligand-stabilized clusters and colloids more and more turn out to act as novel and very instructive subjects of study, especially

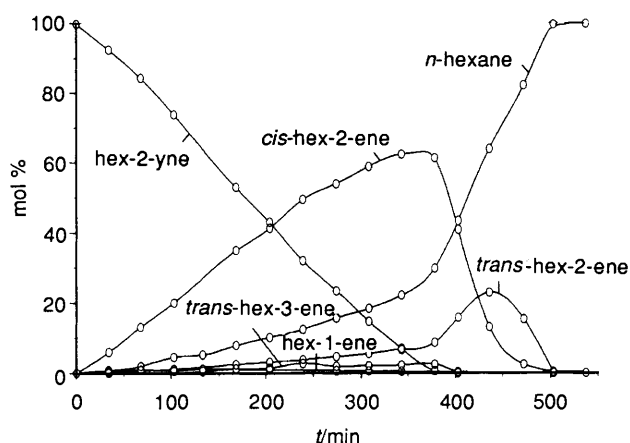


Fig. 10 Hydrogenation of hex-2-yne by 3.8 nm rhodium colloids (1–1.5 wt%) on active carbon

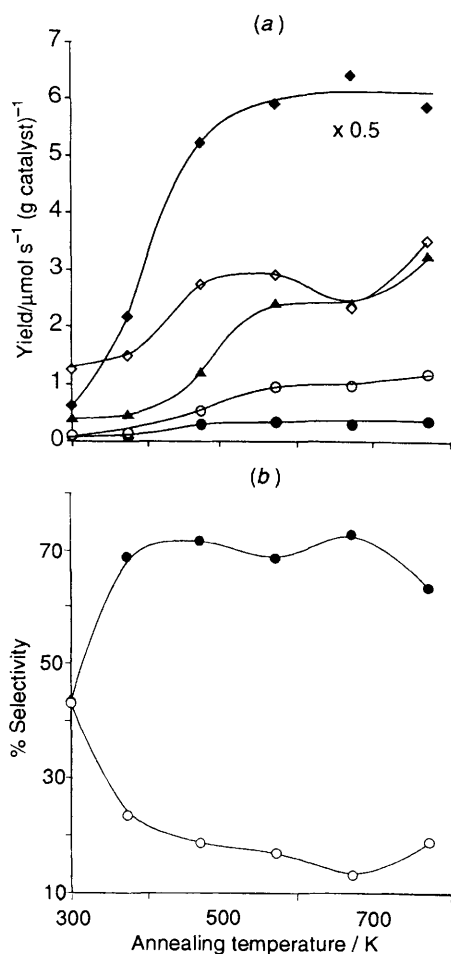


Fig. 11 (a) Correlation between preannealing temperature and products from acetylene oligomerization over Au/Pd colloids: \blacktriangle , isobutene; \bullet , trans-but-2-ene; \circ , cis-but-2-ene; \diamond , n-hexane; \blacklozenge , benzene. (b) C_6 Product (\bullet , benzene; \circ , n-hexane) formation from acetylene over Au/Pd colloids

in heterogeneous catalytic reactions. Compared with traditional metal catalysts, the 'molecular nature' of these materials enables their characterization before supporting. Furthermore, the small size distributions allow conclusions to be made as to the correlation of catalytic activity and particle size. Finally, and this might be the most important advantage, the tailoring of the ligand shell to control selectivity enables novel developments. Though we are still at the very beginning of such developments the future of catalysis carried out with ligand-protected 'quantum dots' looks quite promising.

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