Chemical Catalysis by Colloids and Clusters

L. N. Lewis

General Electric Research & Development, Schenectady, New York 12301

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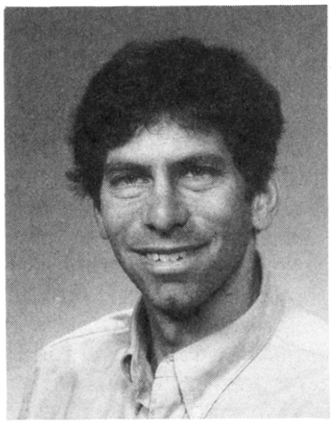
Contents



Larry N. Lewis was raised in New York City and received his B.S. from the State University of New York at Stony Brook in 1976. He earned his Ph.D. in Inorganic Chemistry from Ken Caulton at Indiana University in Bloomington in 1980. His thesis work involved early transition metal cyclopentadienyl metal carbonyl compounds and their small molecule reactivity. Dr. Lewis has been a staff chemist at the General Electric Corporate Research and Development Center in Schenectady, NY, since 1982. Recent research has included studying the fundamentals of the metal-catalyzed hydrosilylation reaction. Larry Lewis is married to science writer and Ph.D. geneticist Ricki Lewis, and they have three daughters: Heather, Sarah, and Carly. Other interests include running and guitar playing. This review is dedicated to the author's father, Benjamin Lewis.

Introduction

Aim and Scope

This review will cover catalysis by metal clusters and colloids. Any system that is a continuous phase is considered. Specifically *not* covered will be supported catalysts or heterogeneous catalysts except as they serve as comparative examples.[1,2] Polymer-stabilized clusters and colloids are considered if they are "soluble." The review will roughly cover the period from 1980 to mid-1992. Essential to this review is the establishment of definitions for the terms cluster and colloid. There are certain intuitive definitions for "cluster" and "colloid." Recent work discussed below shows that the terms cluster and colloid are not clearly distinguishable. This review will use cluster and colloid interchangeably. However, several studies describe methods for distinguishing homogeneous from heterogeneous catalysts, where heterogeneous catalysts may include colloids. For purposes of this review, a heterogeneous catalyst is defined as one where the catalyst is a separate phase, usually a filterable solid from a liquid phase. The distinction between mononuclear or low nuclearity clusters and large clusters or colloids does not necessarily distinguish homogeneous from heterogeneous catalysts. Methods for distinguishing whether a reaction is catalyzed by a mononuclear species or one where metal–metal bonds are present will be described.

Catalysis contributes greatly to world industrial output[3,4] (Table 1). While heterogeneous catalysis is responsible for the largest volume of production, homogeneous catalysis has a significant impact in terms of selectivity,[5,6] thus adding tremendous value to the chemical industry.[7–9] Soluble clusters and colloids present unique opportunities for homogeneous catalysis.[10a]

According to one review in 1983, research on catalysis with metal clusters presents three opportunities: (1) modeling of chemisorbed molecules on metal or metal oxide surfaces, (2) generation of mononuclear fragments, and (3) catalysis unique to clusters. A long list of reactions catalyzed by metal clusters includes isomerizations, reductions of multiple bonds, hydroformylation, Fischer–Tropsch synthesis, and the water–

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Table 1. Major Products and Their Catalysts (Reprinted from Ref 3; Copyright 1988 Chapman and Hall, Ltd.)

reactant(s)	product	typical catayst(s)	global production/kg year^{-1}
crude oil	hydrocarbon fuels	platinum/silica–alumina platinum/acidic alumina metal-exchanged zeolites	1×10^{12}
SO_2, O_2	sulfuric acid	V_2O_5	1.4×10^{11}
N_2, H_2	ammonia	Fe	9×10^{10}
NH_3, O_2	nitric acid	Pt/Rh	2.5×10^{10}
CO, H_2	methanol	Cu/ZnO	1.5×10^{10}
C_2H_4, O_2	ethylene oxide	Ag	1×10^{10}
unsaturated vegetable oils, H_2	hydrogenated vegetable oils	Ni	8×10^{9}
C_2H_4	polyethylene	Cr(II), Ti(III)	6×10^{9}
CH_3OH, O_2	formaldehyde	mixed Fe, Mo oxides	5×10^{9}
C_3H_6, NH_3, O_2	acrylonitrile	mixed Bi, Mo oxides	3×10^{9}
o-xylene, O_2	phthalic anhydride	V_2O_5	2×10^{9}
n-butane, O_2	maleic anhydride	V_2O_5	4×10^{8}

gas shift reaction, to name just a few. However, at the point of its publication, this review could name only one reaction that was unique to clusters, namely, selective hydrogenation of internal alkynes to *trans*-alkenes.[10b] A book on catalysis from 1992 claimed that there were only a few well-documented examples of catalysis by intact clusters.[11] In addition, there are reports of interactions of ligands with metal clusters that are unknown for mononuclear compounds,[12] which suggests that unique catalysis based on clusters is a reasonable expectation.[13] On the other hand, several reports propose reactions catalyzed by clusters.[14–17]

Many interesting reactions of small molecules with clusters have been observed,[4,15,18–20] further suggesting that clusters have a high potential for catalysis. The interaction of carbon monoxide with metal clusters has been extensively studied because of its implications in Fischer–Tropsch and related chemistry. A myriad of CO coordination environments and reduced intermediates have been observed on clusters.[21–24] Gas-phase studies have documented the interactions of bare metal clusters with benzene, which has relevance for aromatic C–H activation.[25] Cluster interactions have been documented with olefins and alkynes.[26] Details of the activation of clusters with H_2 have been investigated.[27] Osmium carbonyl clusters have been exploited as models for C–N chemical transformations such as reduction of nitriles and isocyanides.[28] Thus, this review will attempt to show that clusters and colloids do indeed catalyze many classes of reactions. In some cases the multinuclear nature of the catalyst is maintained during catalysis and this multinuclearity imparts special properties, e.g. selectivity, to the catalyst.

Structure of Large Clusters and Small Colloids

Recent structural results make a clear distinction between these regimes difficult. A point exists where the definition of a large cluster and a small colloid overlap. There are now well-documented examples of structures, which formally would have been called clusters, that exceed 20 Å in diameter, while so-called colloids have been reported with diameters less than 10 Å.[29a,b]

A traditional definition of a colloid is elusive. Several physical chemistry texts classically define colloids as suspensions of finely divided particles of one material in a dispensing medium that do not separate on long standing.[30,31] The size ranges of colloids are generally at an upper limit equivalent to the resolution of a light microscope and a lower limit around 10 Å. Another commonly encountered term, "sol," refers to the suspension of the colloid in a medium.[30,36] Colloidal properties are dominated by their surface due to their small size.[31,32] However, a recent article on clusters used the same definition.[33] Materials which fall under the classification of colloid[34] include foams, emulsions, fogs, aerosols, smokes, miscelles, and macromolecules, including polymers.[30,31,35,36]

Table 2. Close-Packed *n*-Shell Clusters

n	atoms in *n*th shell	total number atoms	*n*	atoms in *n*th shell	total number atoms
1	12	13	4	162	309
2	42	55	5	252	561
3	92	147			

A cluster can be defined as a molecule with two or more metal–metal bonds. One distinction between clusters and colloids may be that colloidal solutions represent a distribution of particle sizes in solution whereas a cluster is a discrete molecular entity. However, the procedure used to synthesize, for example, osmium carbonyl clusters, gives a distribution of "clusters."[37a] Pyrolysis of $Os_3(CO)_{12}$ in a sealed tube at 210 °C gave a mixture (with relative percents in parentheses): $Os_6(CO)_{18}$ (80), $Os_5(CO)_{16}$ (7), $Os_7(CO)_{21}$ (10), and $Os_8(CO)_{23}$ (2).[37a] Other examples of these types of mixtures in metal cluster pyrolyses have been reported.[37b,c] Absolute yield is rarely discussed in these preparations and presumably higher nuclearity clusters form but are not isolated.

Several reports have contributed a rationale to understanding the genesis of clusters. If a cluster forms according to packing rules found in the actual metals (cubic, ccp, or hexagonal, hcp), a single metal atom is surrounded by an icosahedron of 12 atoms, to give a 13-atom cluster. In this way, each shell consists of $10n^2 + 2$ atoms. So-called magic numbers of clusters are built in this way[38] (see Table 2).

The remarkable fact is that structural examples now exist for all of the clusters in Table 2. Several single-crystal X-ray structures have been reported for M_{13} clusters (Figure 1). Larger clusters can form by adding additional shells or by forming clusters of clusters[38,39a,b] (Figure 2). One example is the 38-metal atom framework in $(p\text{-Tol}_3P)_{12}Au_{18}Ag_{20}Cl_{14}$ (Figure 3). This cluster can be described as three gold-centered Au_7Ag_6 icosahedra sharing three corners in a triangular arrangement, giving rise to a $3 \times 13 - 3 = 36$ metal atom cluster. In

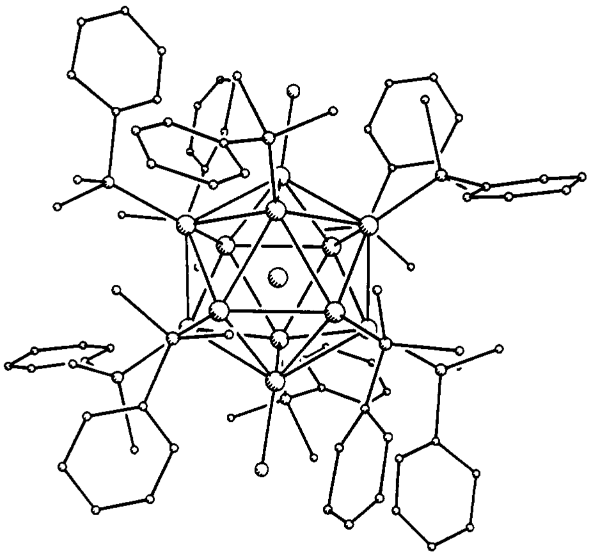


Figure 1. Example of a 13-atom icosahedral Au_{13} cluster. (Reprinted from ref 37; copyright 1988 Pergamon Press, Ltd.)

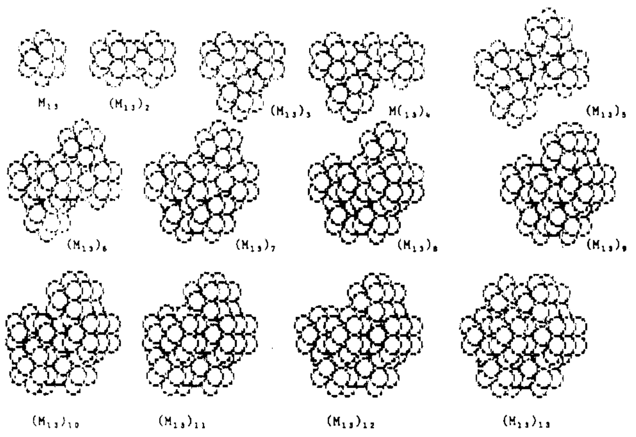


Figure 2. Formation of $(M_{13})_{13}$ cluster of clusters. (Reprinted from ref 37; copyright 1988 Pergamon Press, Ltd.)

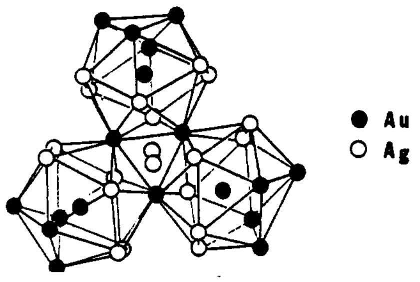


Figure 3. The metal framework of the 38-atom cluster $(p\text{-}Tol_3P)_{12}Au_{18}Ag_{20}Cl_{14}$ (not all metal–metal bonds shown). (Reprinted from ref 38; copyright 1988 Pergamon Press, Ltd.)

this particular example, the entire cluster is capped by two additional silver atoms.

Extensive electron counting rules for clusters of clusters have been developed.[39a] The structures for low molecularity clusters can be rationalized via the topological electron counting (TEC) rule, whose basic assumptions are summarized in Figure 4. The parameter "B" is the number of filled bonding cluster orbitals. The total number of topological electrons, T, is given by eq 1

$$T = V_n + 6V_m + B \qquad (1)$$

where V_n and V_m are described in Figure 4. The "B" parameter is familiar as the number of skeletal electron pairs (SEP) as described by Wade's rules.[40,41]

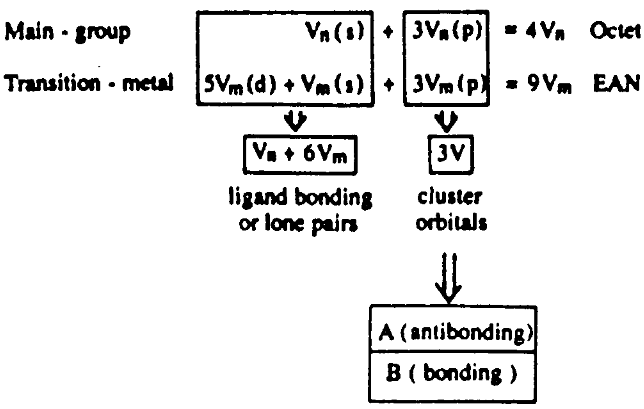


Figure 4. Basic assumptions of the topological electron counting rule: partition of valence orbitals of a cluster containing $\bar{V}$ main I group and V_m transition metal atoms ($V = V_n + V_m$). (Reprinted from ref 39; copyright 1990 Pergamon Press, Ltd.)

For large clusters of clusters of the type listed in Table 2, B values are calculated by taking into account the number of shared vertice(s), edge(s), or face(s). In this way, the large number of observed clusters can be rationalized. Representative clusters are given in Table 3.[42]

Proven examples of clusters of higher nuclearity than those in Table 3 have recently been published. The $n = 2$, 55-atom clusters have been demonstrated for M = Au,[43] Pt,[44] and Ru.[45] The structure of $Ru_{55}(P\text{-}tBu_3)_{12}Cl_{20}$ as determined by HREM (Figure 5) also reveals phase change of the Ru_{55} cluster under influence of an electron beam.

Large clusters have been structurally characterized by a variety of techniques. A single-crystal X-ray structure for a cluster containing 70 Cu atoms has recently been reported. This cluster has 960 valence electrons![47] The $n = 4$ platinum cluster (see Table 2) $Pt_{309}Phen_{36}{}^*O_{30\pm10}$ has been characterized by HREM and X-ray powder diffraction where Phen* is a 1,10-phenanthroline containing p-sodium phenyl sulfate linkages at the 4,7 positions.[48] This cluster had a diameter of 17.5 ± 1 Å (Figure 6).

A cluster with $n = 5$ shells has been well-characterized and has the approximate formula $[Pd_{561}Phen_{60}O_{60}][PF_6]_{60}$. The structure was confirmed by TEM, SAXS, EXAFS, IR, ED, and magnetic susceptibility measurements.[49] Table 4 shows the particle diameter, d(A), as determined via three different techniques. The Pd–Pd distances of 2.60 ± 0.04 Å as determined by EXAFS agreed with those found in the metal. An idealized view of the structure is shown in Figure 7.

The distinction between clusters and colloids is rendered more difficult now that these large cluster entities have been identified. Several microscopy studies have been reported for materials that classically are described as colloids. However, the size range clearly overlaps with the clusters described above.[50] The distinction between cluster[52] and colloid based solely on size cannot be valid.[51–55] Synthetic techniques for colloids usually require reduction to generate metal crystallites,[51,56–60] which are then stabilized against agglomeration. Often the colloid's stabilizers differ from cluster's ligands only in their complexity. These

Table 3. Packing Type, Number of Bulk (m_b) and Surface (m_s) Atoms, Number of Electrons per Bulk (n_b) and Surface (n_s) Atoms, and Calculated (N_{calc}) and Observed (N_{obs}) Electron Counts for a Number of Close-Packed High-Nuclearity Metal Clusters (Reprinted from Ref 42; Copyright 1983 the Royal Society of Chemistry)

no.	cluster	packing	m_b	m_s	n_b	n_s	N_{calc}	N_{obs}	% error[a]
1	$[Rh_{13}(CO)_{24}H_{5-q}]^{q-}$ ($q = 2$,[e] 3,[f] 4[g])	hcp[b]	1	12	11.75	13.22	170.4	170	0
2	$[Rh_{14}(CO)_{25}H_{4-q}]^{q-}$ ($q = 3$,[h] 4[i]) $[Rh_{14}(CO)_{26}]^{2-}$ [j]	incomplete bcc[c]	1	13	11.50	12.94	179.7	180	0
3	$[Rh_{15}(CO)_{27}]^{3-}$	bcc/hcp	1	14	11.50	12.94	192.6	192	0
4	$[Rh_{15}(CO)_{30}]^{3-}$	bcc	1	14	11.50	12.94	192.6	198	−3
5[m]	$[Rh_{17}(CO)_{30}]^{3-}$	hcp	1	16	11.75	13.22	223.3	216	3
					11.24	12.64	213.5	216	1
6[n]	$[Rh_{22}(CO)_{37}]^{4-}$	fcc/hcp	1	21	11.24	12.64	276.7	276	0
7[o]	$[Rh_{22}(CO)_{35}H_{5-y+z}]^{q-}$ ($q = 4, 5$)	fcc/bcc	2	20	11.24	12.64	275.3	$273 + x$	–
8[p]	$[Pt_{19}(CO)_{22}]^{4-}$	pentagonal	2	17	11.17	12.56	235.9	238	−1
9[r]	$[Pt_{24}(CO)_{30}]^{2-}$	fcc[d]	1	23	11.24	12.64	301.9	302	0
10	$[Pt_{26}(CO)_{32}]^{2-}$	hcp	3	23	11.75	13.22	339.3	326	4
					11.24	12.64	324.4	326	0
11[r]	$[Pt_{38}(CO)_{44}H_2]^{2-}$	fcc	6	32	11.24	12.64	471.9	472	0
12[s]	$[Au_{13}(PMe_2Ph)_{10}Cl_2]^{3+}$	icosahedral	1	12	11.17	12.56	161.9	162	0

[a] Percent error = $100 \times (N_{calc} - N_{obs})/N_{obs}$. [b] Hexagonal close-packed. [c] Body-centered cubic. [d] Face-centered cubic. [e–s] See ref 42 for remaining footnotes.

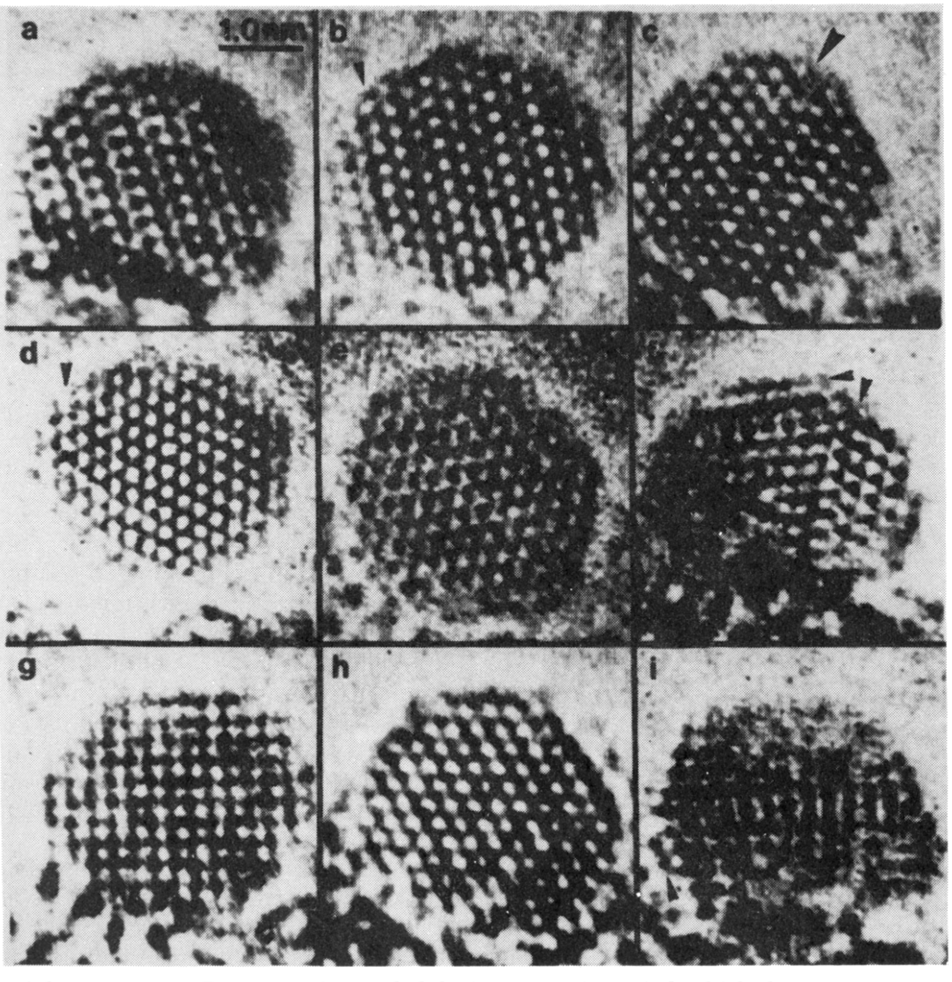


Figure 5. Images of the same 3-nm, Ru_{55} crystal recorded during a 30-min period, which show rearrangements in the crystal structure and the occurrence of four basic structure types: (a) The hcp structure, (b) disordered hcp structure, (c) half hcp and half ccp structure (The $\overline{111}$ plane separating the two structures is marked with an arrow.), (d) mostly ccp, except for three/four planes (at left) which show hcp stacking, (e) all ccp structure, (f) defects and twinning (marked with arrow) in ccp structure, (g) bcc structure. View along $\overline{100}$. (h) bcc structure viewed along $\overline{111}$, (i) multiply twinned icosahedral stacking. (Reprinted from ref 45; copyright 1988 VCH Verlagsgesellschaft mbH.)

stabilizers include polymers,[55,61–90] microemulsions,[91–99] colloidal polymers,[100] monomers,[101] solvents,[102–105] sol gel,[106] and clays.[107] Furthermore, most materials considered colloidal contain stabilizing media, polymers, solvents, etc. Only a lack of detailed structural knowledge of metal colloid surfaces distinguishes these

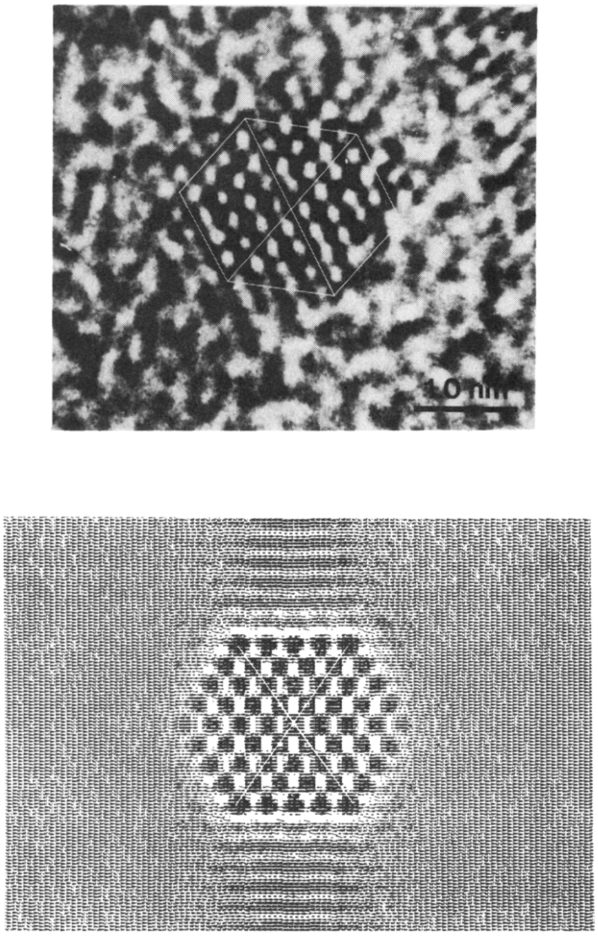


Figure 6. Top: HREM of a four-shell Pt cluster in the $\overline{110}$ direction. Bottom: computer simulated image of an M_{309} cluster in the $\overline{110}$ direction. (Reprinted from ref 48; copyright 1989 VCH Verlagsgesellschaft mbH.)

Table 4. Metal Skeleton Size for the Pd_{561} Cluster as Evaluated by Three Techniques (Reprinted from Ref 49; Copyright 1989 Elseiver Sequoia S. A.)

method	d (Å)
TEM	26 ± 3.5
ED	~25
SAXS	20 ± 5

materials from a cluster which contains ligands such as phosphine, CO, Phen.[108]

Mixed-metal colloids of $Pt_{100-x}Au_x$ were prepared and analyzed by STEM. This analysis showed a narrow size distribution for the diameter, d, of these mixtures: $x = 0$, $d = 23 \pm 9$ Å; $x = 10$, $d = 48 \pm 18$ Å; $x = 50$, $d = 123 \pm 14$ Å; $x = 90$, $d = 143 \pm 40$ Å; and $x = 100$, $d = 247 \pm 64$ Å.[109] These colloids can be considered as a large distribution of clusters. Materials traditionally characterized as colloids were recently shown to follow a common agglomeration pattern, whether they are gold, silica, or polystyrene.[110]

The mixed platinum–gold colloids described above were prepared via citrate reduction of the salts H_2PtCl_6 and $HAuCl_4$. Presumably charge–charge repulsion stabilized by citrate contributes to the colloidal stability. If an all gold colloid made via citrate reduction is reacted with a "water-soluble ligand", $(C_6H_5)_2PC_6H_4SO_3Na$, then the "cluster" could be isolated as a precipitate and redissolved. Several analyses, including TEM, showed that the gold cluster had a diameter of 186 ± 10 Å.[111]

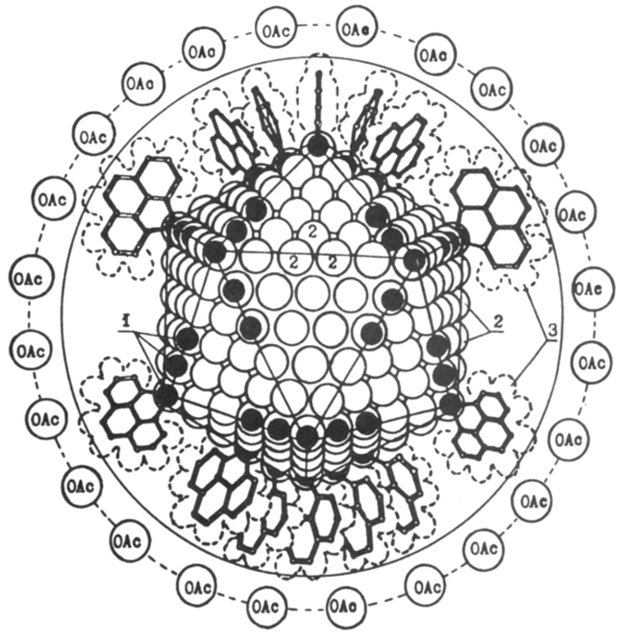


Figure 7. Idealized model for the Pd_{561} cluster. 1 = Pd atoms coordinated with Phen ligands. 2 = Pd atoms accessible for coordination by OAc^-, substrate, or solvent molecules. 3 = van der Waals' shapes of coordinated phen molecules. (Reprinted from ref 49; copyright 1989 Elsevier Sequoia S. A.)

This work concluded with the phrase, "gold colloids can be regarded as extremely large clusters". So-called Pt colloids, stabilized by PVP and prepared in butanol, can be reversibly transferred into organic and aqueous media.[112] In this work the terms colloid and cluster were used interchangeably.[113] These properties certainly remind one of those ascribed to a cluster.

Mixed Pt/Rh and Rh/Au colloids were prepared in the presence of a polymer stabilizer. TEM analyses showed 28–40 Å particles. PVP-stabilized platinum colloids have been analyzed by HREM and EXAFS.[114] This approach permits a second in situ approach to complement the HREM analysis. Microscopic analyses require evaporation of solutions on a grid where agglomeration could occur. TEM analysis showed an average particle diameter of 26 Å with most particles having a nearly perfect fcc lattice (hexagonal as viewed down the 110 direction). The EXAFS analyses of solutions of these colloids were compared to data taken for bulk platinum metal. A close correlation between the Fourier transforms of the EXAFS for the colloidal Pt and bulk metal confirmed the presence of fcc crystallites in solution. At least one other EXAFS analysis has been reported for polymer-stabilized colloids.[115]

Many other techniques have been used to analyze clusters.[116] Multinuclear NMR has been used under a high pressure of CO to identify the cluster products from $[Rh_4(CO)_{12-x}L_x$ ($L = P(OPh)_3$, $x = 1$–4).[117] The use of UV–VIS absorption spectroscopy has been used for many years to analyze metal colloids. A recent article evaluated this technique for over 12 different metal colloids.[118]

High-resolution ^{13}C NMR spectroscopy was applied to analyze the surface of CO-containing PVP-stabilized palladium colloids.[29a] With colloids larger than 20 Å in diameter, the material becomes metallic, causing a

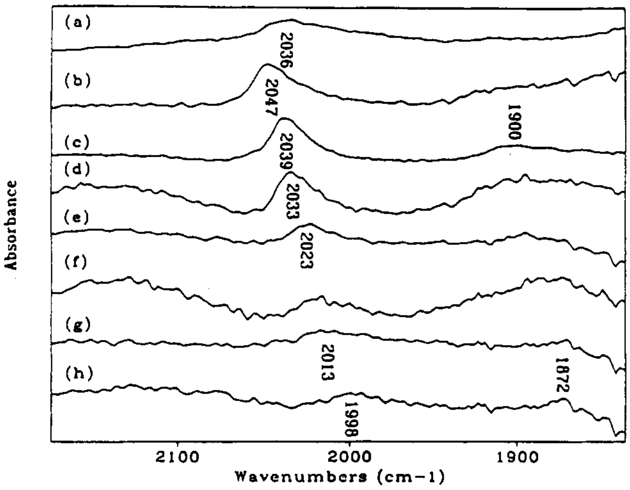


Figure 8. A series of IR spectra of CO adsorbed on a Rh hydrosol at pH (A) 0.41, (B) 1.51, (C) natural pH (2.2), (D) 3.78, (E) 6.80, (F) 8.29, (G) 9.86, and (H) 11.35. (Reprinted from ref 84; copyright 1991 the American Chemical Society.)

large Knight shift. However, observation of the free CO peak by ^{13}C NMR using spin saturation transfer permitted indirect analysis of the Pd-colloid-bound CO. Although not directly observed, the bound CO resonance was estimated to be at 800 ppm for a 70 Å diameter colloid.

IR analysis was applied to study the surface of CO bound to a platinum colloid.[29b] Aluminoxane-stabilized platinum colloids had an upper particle diameter of 8 Å, which placed these metal particles in a size range comparable to the core sizes of some of the larger molecular carbonyl clusters. IR data showed that, for bound carbon monoxide, the CO stretch shifted to lower frequency as the cluster size decreased. Evidence from these studies suggested that reaction of the colloid with CO produced species with identical IR spectra to known platinum clusters. Interconversion of colloid to cluster would appear to require nothing more than a ligand exchange, aluminoxane for CO.

Other IR studies of the product of CO with a platinum colloid have been reported[119] as have other techniques employed as probes to study CO bound to Rh colloids.[84] IR analysis determined that PVA-stabilized Rh colloids did not contain *gem*-dicarbonyl species, but did contain linear and bridge CO ligands. Infrared analysis of PVA-stabilized Rh colloids with adsorbed CO was also carried out at different pH levels. The natural pH of these materials was defined as the pH of the solution following preparation of the Rh colloid from borohydride reduction of $RhCl_3$ in an aqueous PVA solution followed by ion exchange. The carbonyl stretching frequency generally shifts to lower energy as pH is increased from the natural pH of 2.2. In addition, overall CO coverage decreases with increasing pH as CO competes for binding sites with growing oxide and hydroxide species (Figure 8).

Mass spectroscopy was, until recently, limited to molecular weights of only a few thousand amu. The technique of ^{252}Cf plasma desorption mass spectroscopy (^{252}Cf-PDMA) has permitted detection of giant clusters.[120] This technique was applied to the gold cluster $Au_{55}(PPh_3)_{12}Cl_6$.[121] Surprisingly, none of the observed high mass zones corresponded to the Au_{55} cluster, as suggested originally[122] (Figure 9). The observed mass zones were explained on the basis of vertex sharing icosahedra, I.[123] Therefore, the observed mass zone at about 16 000 m/z was consistent with I_6 or $Au_{67}(PPh_3)_{14}Cl_8$. The other observed mass zones were similarly explained.

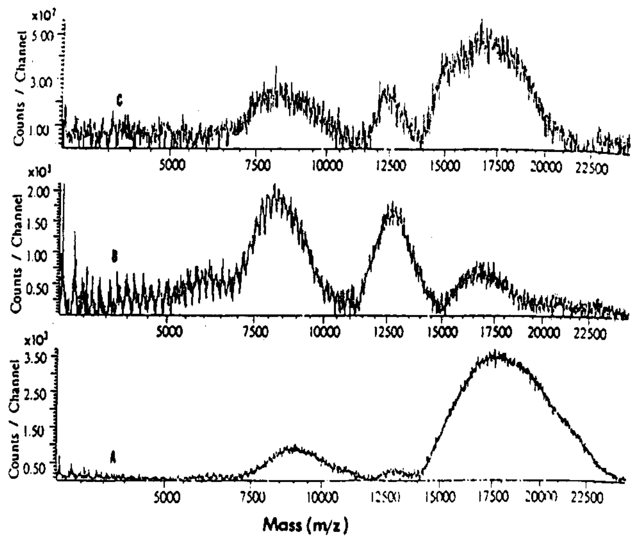


Figure 9. ^{252}Cf plasma desorption positive ion mass spectra of three different preparations (A, B, C) of $Au_{55}(PPh_3)_{12}Cl_6$ showing the three high mass zones of high intensity. (Reprinted from ref 121; copyright 1989 the American Chemical Society.)

Onset to Metallic Properties

Cluster catalysis is further anticipated by the close correlation of properties between clusters and bulk metal.[124,125] Several authors attempt to determine the size of clusters at which the onset of metallic properties occur. This discussion also adds confusion when trying to distinguish between clusters and colloids.[126] One recent study describes clusters as <1000 atoms or 25 Å diameter.[116] These dimensions clearly encompass those included for colloids.

The three-dimensional arrangement of atoms in some large clusters, such as $[Pt_{38}(CO)_{44}H_x]^{2-}$, generally models the packing found in bulk crystals with only relatively few exceptions.[50,127] Metal–metal bond distances of some clusters closely match those found in the bulk (Table 5). Several giant clusters have properties which exactly correspond to small metal crystallites.[38,126]

Magnetic properties can determine the onset of metallic properties for small clusters. For example, in the series of clusters from $Os_3(CO)_{12}$ and $H_2Os_{10}C(CO)_{24}$,

Table 5. Metal–Metal Bond Distances in Bulk Crystals and Clusters (Reprinted from Ref 127; Copyright 1986 Elsevier Science Publishers)

metal or cluster	metal–etal bond distance (nm)	metal or cluster	metal–metal bond distance (nm)
Fe bulk (bcc)	0.249	$Rh_6(CO)_{16}$	0.278
$Fe_4(CO)_{13}^{2-}$	0.255	$Rh_4(CO)_{12}$	0.273
Os bulk (bcp)	0.268	Ir bulk (fcc)	0.271
$Os_6(CO)_{18}^{2-}$	0.268	$Ir_4(CO)_{12}$	0.269
Co bulk (hcp)	0.251	$H_2Ir_4(CO)_{10}^{2-}$	0.276
$Co_4(CO)_{12}$	0.249	Ni bulk (fcc)	0.249
$Co_6(CO)_{15}^{-2}$	0.251	$(\eta^5\text{-}C_5H_5)_4Ni_4H_3$	0.246
Rh bulk (fcc)	0.269	$Ni_4(CO)_6[P(CH_2CH_2CN)_3]_4$	0.251

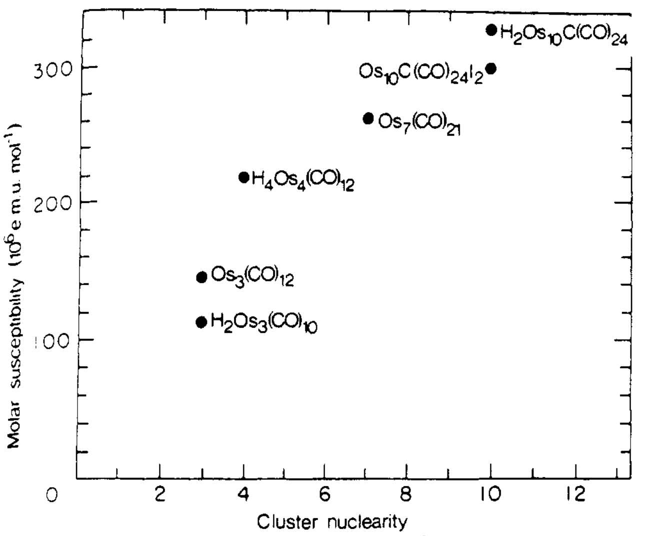


Figure 10. Magnetism in Os cluster carbonyls. The variation of the high-temperature (298 K) excess molecular susceptibility, κ_{ems}, as a function of cluster nuclearity. (Reprinted from ref 128; copyright 1985 MacMillan Magazines, Ltd.)

the onset of metallic properties occurs as a function of the excess molecular susceptibility, κ_{ems}. This represents the difference between the magnetic susceptibility of the cluster and the sum of the magnetic susceptibility of those species from which the complex is composed; e.g. for $H_2Os_{10}C(CO)_{24}$, it is the sum of H, Os, C, and CO. The results from this study are shown in Figure 10.[128] In terms of its magnetic properties, $H_2Os_{10}C(CO)_{24}$ may be representative of a small metallic particle.[129] Similar measurements and conclusions have been made for nickel clusters containing 32 and 44 atoms (Figure 11).[130] The authors concluded that bare Ni_n clusters containing as few as tens of atoms exhibit some of the features of bulk metal. The Pd_{561} cluster (Figure 7) has magnetic susceptibility properties similar to that for bulk Pd.[131]

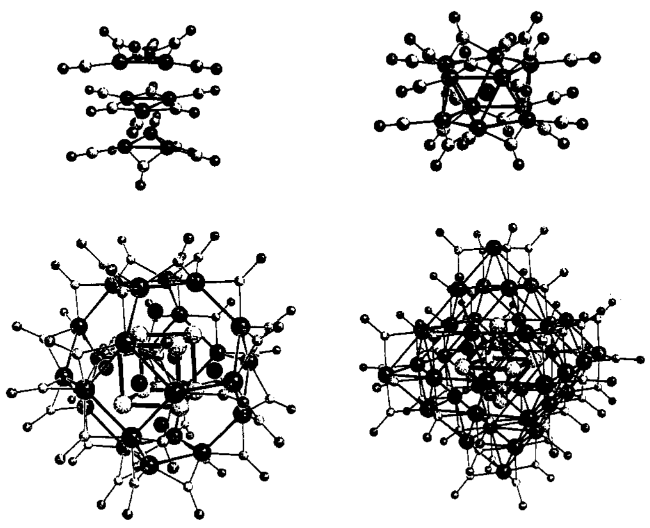


Figure 11. Geometry of the $[Ni_9(CO)_{18}]^{2-}$, $[Ni_{10}Ge(CO)_{20}]^{2-}$, $[Ni_{32}C_6(CO)_{36}]^{n-}$, and $[Ni_{44}(CO)_{48}]^{n-}$ clusters. (Reprinted from ref 130; copyright 1992 the Americal Chemical Society.)

The measurement of the UV–VIS spectrum for colloidal solutions has been one of the traditional methods of their analysis. The absorption bands are due to plasma resonances or interband transitions. These bands are characteristic of the metallic properties of colloids. An extensive study has recently appeared for the absorption spectra for 100-Å particles of 52

Table 6. Ionization Thresholds of Transition Metal Clusters (eV) (reprinted from ref 132; copyright 1986 the American Chemical Society.)

n	V_n[a]	Fe_n[b]	Ni_n[c]	Cu_n[d]	Nb_n[a,e]
1	6.74[f]	7.90[f]	7.633[f]	7.724[f]	6.77[f]
2	6.10 ± 0.05	6.30 ± 0.01	7.1 ± 0.7[g]	7.894 ± 0.015	–
3	5.49 ± 0.05	6.45 ± 0.05	6.0 ± 0.4	5.78 ± 0.20[h]	–
4	5.63 ± 0.05	6.40 ± 0.10	6.0 ± 0.4	7.15 ± 0.75	5.58 ± 0.05
5	5.47 ± 0.05	5.95 ± 0.05	6.0 ± 0.4	5.99 ± 0.41	5.43 ± 0.05
6	5.37 ± 0.05	5.90 ± 0.10	7.15 ± 0.75	7.15 ± 0.75	5.34 ± 0.05
7	5.24 ± 0.05	5.75 ± 0.05	6.0 ± 0.4	5.99 ± 0.41	5.32 ± 0.05
8	5.36 ± 0.05	5.65 ± 0.05	6.0 ± 0.4	5.99 ± 0.41	5.46 ± 0.05
9	5.20 ± 0.05	5.45 ± 0.05	6.0 ± 0.4	5.28 ± 0.30	4.93 ± 0.05
10	5.17 ± 0.05	5.37 ± 0.10	6.0 ± 0.4	5.28 ± 0.30	5.33 ± 0.05
11	4.99 ± 0.05	5.35 ± 0.05	6.0 ± 0.4	5.28 ± 0.30	4.72 ± 0.05
12	4.95 ± 0.05	5.45 ± 0.05	6.0 ± 0.4	5.28 ± 0.30	4.91 ± 0.05
13	4.93 ± 0.05	5.50 ± 0.05	6.0 ± 0.4	5.28 ± 0.30	4.84 ± 0.05
14	4.96 ± 0.05	5.65 ± 0.05	6.0 ± 0.4	5.28 ± 0.30	4.65 ± 0.05
15	≤4.70	5.60 ± 0.10	6.0 ± 0.4	5.28 ± 0.30	≤4.60
16	4.99 ± 0.05	5.55 ± 0.05	6.0 ± 0.4	5.28 ± 0.30	4.76 ± 0.05
17	5.00 ± 0.05	5.50 ± 0.05	6.0 ± 0.4	5.28 ± 0.30	≤4.60
18	4.91 ± 0.05	5.55 ± 0.10	6.0 ± 0.4	5.28 ± 0.30	4.60 ± 0.05
19	≤4.70	5.25 ± 0.05	6.0 ± 0.4	5.28 ± 0.30	≤4.60
20	≤4.70	5.25 ± 0.05	6.0 ± 0.4	5.28 ± 0.30	≤4.60
21	≤4.70	5.25 ± 0.05	6.0 ± 0.4	5.28 ± 0.30	≤4.60
22	≤4.70	5.25 ± 0.05	6.0 ± 0.4	5.28 ± 0.30	≤4.60
23	–	5.15 ± 0.15	6.0 ± 0.4	5.28 ± 0.30	4.67 ± 0.05
24	–	5.15 ± 0.15	6.0 ± 0.4	5.28 ± 0.30	4.73 ± 0.05
25	–	5.15 ± 0.15	6.0 ± 0.4	5.28 ± 0.30	4.68 ± 0.05
26	–	–	–	–	4.77 ± 0.05
27	–	–	–	–	4.67 ± 0.05
28	–	–	–	–	4.60 ± 0.05
–					
–					
∞	4.12[i]	4.31[i]	4.50[i]	4.4[i]	3.99[i]

[a–i] See Table 26 of ref 132 for the original footnotes.

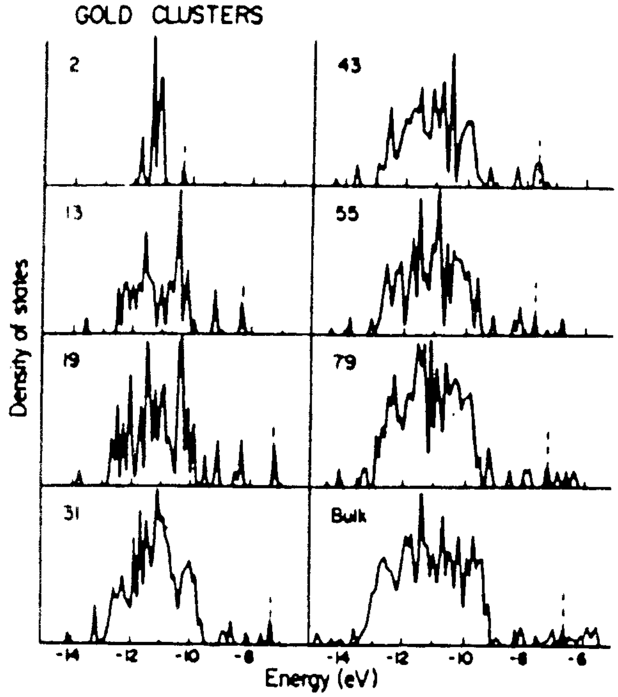


Figure 12. DOS plots for fcc spherical gold clusters. (Reprinted from ref 136; copyright 1981 the American Chemical Society.)

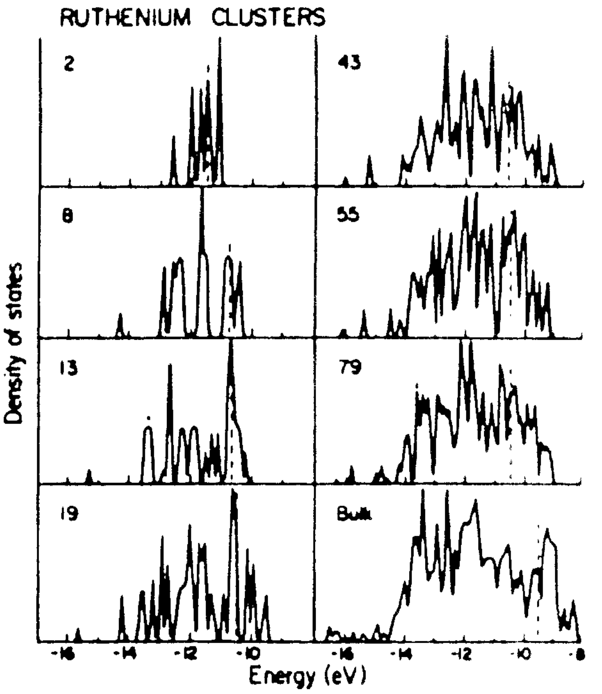


Figure 13. DOS plots for fcc spherical ruthenium clusters. (Reprinted from ref 136; copyright 1981 the American Chemical Society.)

different elements.[116] For example, a cluster composed of a $Ag_{20}Au_{18}$ core has a UV spectrum indicative of free electron behavior.

Onset of metallic properties of small clusters has been examined by measurement of metallic band structure.[132,133] Ionization thresholds of transition metal clusters have been tabulated for several metals of n size (M_n) and compared to bulk values (Table 6).[132] Metallic properties appear to begin at $n \geq 20$. Other studies have employed various techniques[134] to establish a density of states (DOS) profile as a means to determine metallic properties as a function of cluster size. For copper and palladium, metallic properties begin around cluster sizes of 40.[135] A typical DOS plot is shown in Figures 12 and 13 for gold and ruthenium clusters, respectively, with additional data for Ag, Au, Ru, and Pd shown in Table 7.[136]

Perhaps more germane to this review are the studies where the particle size of clusters is correlated to onset of catalytic activity observed for bulk metal heterogeneous catalysts. Most work has concentrated on supported catalysis.[11,137-143] An early study of silver atoms showed via MO calculations and ionization potential and electron affinity measurements that 20 atoms were the minimum size for onset of catalytic properties.[145] Other theoretical studies for hydrogenation on platinum showed optimized size at four to eight atoms.[146]

Justification of the use of clusters as catalysts is well-supported by the above discussion. Metal carbonyl clusters feature prominently in many studies. One report showed a close similarity of the bonding of CO to a Pd surface and Pd_n cluster.[147] In the late 1970s and early 1980s, the prevailing opinion was that clusters had not yet provided catalysts with any unique activity or selectivity.[10,148-150]

Despite the apparent lack of success in the early cluster catalysis work, clusters and colloids have played an important role in the 1980s. A summary of the impact of clusters in Fischer–Tropsch catalysis has recently been published.[151] Furthermore, a new concept, that of "surface organometallic chemistry," has recently emerged.[124,152,153] It is well-established that clusters can act as a source of small particles.[152] A 1990 report does state, "Not in any case could it be shown that the starting cluster itself works as a catalyst".[126] This statement is contradicted by reviews[15] which cite a number of examples of cluster catalysis. Hopefully, examples provided below will serve to support the second position.

Table 7. HOMO Value (eV) Calculated for Metals Clusters (Reprinted from ref 136; copyright 1981 the American Chemical Society.)

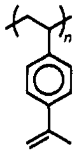
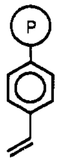
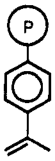
size	Ag	Au	Ru	Pd
2	8.60	10.28	11.06	10.58
13	7.07	8.13	10.65	10.31
19	6.63	7.43	10.52	10.11
31	6.67	7.29	10.66	9.96
43	6.63	7.60	10.63	9.89
55	6.75	7.68	10.54	9.95
79	6.51	7.28	10.55	9.89
bulk	6.17	6.70	9.70	9.60

The most inspiring and exciting result in cluster catalysis regards the work on giant palladium clusters. Oxidation of a Pd_4 cluster gave the $n = 5$ Pd_{561} cluster described above.[154] This giant cluster was an active catalyst for the oxidative acetoxylation of olefins.[155]

Mononuclear vs Cluster Catalysis

This review is concerned with catalysis by clusters or colloids. A reaction may employ a mononuclear precursor which forms a cluster under catalytic conditions.[156] Several examples of the converse situation are known, namely, a cluster precursor yielding mononuclear active species.[14] Finally, mononuclear and/or

Table 8. Olefin Hydrogenation[a] (Reprinted from Ref 162; Copyright 1984 the American Chemical Society.)

run	catalyst	monomers		soluble polymers		cross-linked polymers			ref
					 [b]	 [c]	 [d]	 [e]	
1	$RhCl(PPh_3)_3$	100	100	30[f]	100	100	100	100	33
2	$[Rh(NBD)(PPh_3)_2][ClO_4]$	100	100				90		34
3	$[Rh(NBD)(PPh_3)_2][ClO_4] + NEt_3$		100				65		34
4	5% Pd/C	100	100	[5][i]	[5]	[0]	[0]	[0]	31
5	5% Rh/Al_2O_3		100			[0]	[3]		31
6	$Ni(acetate)_2$[g] + NaH + ROH	100	100		3–22		[5]	[0]	36
7	$Ni(2\text{-ethylhexanoate})_n + NaBH_4$	100	100	30		[0]	[4]		
8	$Co(2\text{-ethylhexanoate})_n$[h] + nBuLi		100				20		37

[a] Values given in the table are the percent olefin hydrogenated under the following conditions: 3.0 μmol of catalyst, 300 μmol of olefin, 5 mL of solvent, room temperature, 1–2 atm of hydrogen, 24 h unless otherwise indicated. [b] 1.33 mequiv/g. [c] 1% cross-linked beads, 0.99 mequiv/g. [d] 1% cross-linked polystyrene beads, 1.74 mequiv/g. [e] Macronet isoporous resin, 1.56 mequiv/g. [f] 0.5 h. [g] 30 μmol of catalyst, 600 μmol of olefin. [h] 50 μmol of catalyst, 5 mmol of olefin monomer, 300 μmol of olefin polymer, 50 °C, 50 psig hydrogen, 8 h. [i] Values in brackets are equal to zero within the limited accuracy of the measurement (±5%).

cluster–colloid precursors can degrade to bulk metal under catalytic conditions.[157] The key question is, how can one test for the presence of soluble clusters and colloids?

In a reaction related to Fischer–Tropsch, CO is hydrogenated to give methanol and methyl formate. This reaction is catalyzed by several ruthenium cluster precursors including $H_4Ru_4(CO)_{12}$, $H_3Ru_4(CO)_{12}^-$, $Ru_3(CO)_{12}$, and $Rh_6C(CO)_{16}^{2-}$. All clusters were converted to $Ru(CO)_5$ under catalytic reaction conditions. Kinetic analysis determined a first-order dependence of hydrogenation rate on ruthenium concentration. These data were consistent with involvement of a mononuclear ruthenium complex.[157]

The above kinetic treatment was one of the first to address the question of the nuclearity of a catalytic species. A more in-depth study established five criteria for determining whether a reaction was catalyzed by a cluster:

(1) Catalyst concentration studies wherein the turnover frequency, TF [(TF = moles of product/(moles of catalyst) (unit time)], increases with increasing catalyst concentration are indicative of cluster catalysis.

(2) Product selectivities different from those using mononuclear precursors suggest cluster catalysis.

(3) Unusual or enhanced reactivity of a catalyst composed of two or more metal atoms which differs from the individual metal components indicates cluster catalysis.

(4) If a modification in the reaction conditions favors metal–metal bond formation and this results in increased activity, then metallic cluster catalysis is suspected.

(5) Asymmetric induction, where the asymmetry resides in the metal framework, supports catalysis via clusters.[158a]

Several applications of criterion 1 were described, such as hydroformylation catalyzed by $Ru_3(CO)_{12}$. Analysis of kinetic data, including a TF determination, suggested cluster catalysis. Kinetic data supports formation of mononuclear species from cluster precursors.

Criterion 2, namely, selectivity derived from a cluster but not derived from a mononuclear source, is very difficult to prove. Equivocal conclusions are reached unless all possible mononuclear catalysts are considered. For example, oligomerization of alkynes on $Cp_2Mo_2(CO)_4$ is believed to proceed via cluster catalysis since the reaction does not proceed with any known related mononuclear compound.

Criterion 3 is also difficult to demonstrate. Addition of iron to the $Ru_3(CO)_{12}$-catalyzed hydroformylation of methanol increased the rate but not the selectivity. Definitive proof of mixed metal cluster catalysis in this and other examples was lacking. An additional example was published later for $Ru_3(CO)_{12}$-catalyzed hydrodenitrogenation.[158b]

Criterion 4 is best demonstrated with heteroatom-stabilized clusters. Some clusters such as $[Rh_{17}S_2(CO)_{32}]^{3-}$, $[Rh_9P(CO)_{21}]^{2-}$ and $[Rh_6C(CO)_{15}]^{2-}$ exhibit catalytic activity under conditions where they remain stable.[159]

The final criterion requires synthesis and isolation of a pure racemic cluster such as $Co_2(CO)_6CpW(CO)_2CCH_3$ or $Fe(CO)_3Co(CO)_3CpMo(CO)_2S$. This requirement had not been achieved in the early 1980s but was suggested in a later report.[160]

Other more "direct" techniques have been used to distinguish a multinuclear catalyst from a mononuclear component in a metal-catalyzed reaction. One technique employed the addition of filter-aid (powdered cellulose) to a solution after completion of an ostensibly homogeneous catalyzed reaction. The filter-aid and filtrate were then tested for catalytic activity.[161] One obvious problem with this approach is that extremely small colloids/clusters could pass through the filter-aid. The very point of this review is revealed in this discussion. If the filter-aid removed catalytically active species, the reaction is classified as heterogeneous. However, a catalytically active cluster may pass through the filter-aid. What designation should be given for a reaction catalyzed by a cluster that cannot be filtered but contains many metal atoms? Since the cluster is part of a continuous phase, this would represent homogeneous catalysis mediated by a cluster.

Another technique attempts to distinguish catalysts on the basis of size. In this method, the unsaturated substrate is part of a cross-linked polymer. The premise

Table 9. Experimental Results with dct and Hg Inhibitors (Reprinted from Ref 167; Copyright 1983 the American Chemical Society.)

				rate[d]	
catalyst[a]	inhibitor[b]	temp (°C)	ratio[c]	mL min^{-1}	%[e]
$RhCl(PPh_3)_3$	dct	25	0.0	4.0	100
			0.1	2.5	63
			0.2	1.7	43
			0.5	0.25	20
			1.0	0.0	6
			2.0	0.0	0
	Hg		*f*	4.0	100
$[Ir(cod)(PMePh_3)_2]PF_6$	dct	0	0.0	11.0	100
			0.25	8.5	77
			0.50	5.8	53
			0.75	2.4	22
			1.0	0.0	0
			2.0	0.0	0
	Hg	0	*f*	11.0	100
Pd/C/hexane	dct		0.0	10.9	100
			0.01	10.3	95
			0.1	10.1	93
			0.5	9.8	90
			0.75	8.9	82
			1.0	8.5	78
			10.0	4.6	42
	Hg		*f*	0.0	0
Pd/C/dmf	dct	30	0.0	3.5	100
			1.0	3.0	86
Pd/C/EtOH-H_2O	dct	30	0.0	2.5	100
			1.0	2.0	80
Pd/colloid	dct	25	0.0	2.8	100
			2.0	2.8	100
	Hg		*f*	0.0	0
Rh/colloid	dct	25	0.0	0.5	100
			2.0	0.5	100
	Hg		*f*	0.0	0
$[Rh(nbd)(PPh_3)_2]PF_6$	dct	25	0.0	3.3	100
			2.0	0.0	0
	Hg		*f*	3.3	100
$RuCl_2(PPh_3)_3$	dct	25	0.0	3.0	100
			2.0	0.0	0
	Hg		*f*	3.3	85
$RuCl_3(py)_3/NaBH_4$	dct	25	0.0	1.0	100
			2.0	1.0	100[g]
	Hg		*f*	0.0	0
polymer-bound $RhCl(PPh_3)_3$	dct	25	0.0	14.0[h]	100
			2.0	0.0	0
	Hg		*f*	13.0[h]	93

[a] Catalysts were prereacted with either dct or Hg. [b] Potential inhibitor. [c] Mole ratio based on metal content. [d] Percent H_2 uptake. [e] Percentage of unhibited rate. [f] Excess Hg. [g] Similar results after 48 h of stirring with dct. [h] mL h^{-1}.

is that large catalysts cannot diffuse through the cross-linked matrix while mononuclear or low nuclearity clusters can.[162] Several examples clearly show that mononuclear catalyst precursors are active hydrogenation catalysts for monomeric styrenic substrates and soluble and cross-linked polymers. However, heterogeneous catalysts were not catalytically active for hydrogenation of olefins in the cross-linked polymer. Unfortunately, no clusters or colloids were evaluated in this study (Table 8).[162]

A series of papers discussed hydrogenation and alkane dehydrogenation catalyzed by low valent, late transition metal complexes.[163,164] Three approaches checked for catalysis via colloids in the dehydrogenation of alkanes catalyzed by compounds such as $CpIrH(PPh_3)_2^+$. Mononuclear catalysis was indicated if (1) the selectivity pattern matched that for known mononuclear catalysts, but differs from all known colloidal ones, (2) authentic colloids catalyzed a reaction not catalyzed by the presumed mononuclear catalyst, and (3) light-scattering measurements ruled out the presence of colloids in a few cases[163-165] and showed colloids were present in another case.[166] Nitrobenzene was reduced to aniline in the presence of Ir colloids, but not in the presence of the mononuclear iridium phosphine compound.

Mononuclear and cluster/colloid catalysts can be distinguished from each other by adding selective poisons. Dibenzocyclooctatetraene (dct) has a "tub-shaped" configuration and thus binds strongly to mononuclear metal centers, but not to metal surfaces.[167] Mercury can be added as a selective poison for metal colloids and surfaces.[167,168] A summary of the effect of the dct and mercury tests is shown in Table 9 for a number of mononuclear, colloidal, and supported metal systems.

Mercury apparently forms an alloy with metal surfaces, thus effectively blocking their active sites.[169] However, at least one study shows mercury acceleration of a platinum-catalyzed dehydrogenation reaction where Pt/SiO_2 was the catalyst.[170]

Hydrogenation

Unsupported Colloids

Hydrogenation reactions have been the most extensively studied for measuring the activity of colloids and clusters. Recalling the aims and scope of this review, only homogeneous reactions are described. Stabilization of clusters with ligands or colloids with protective polymers has roughly the same effect, that is to maintain a continuous phase without deposition of bulk metal during catalysis. Hydrogenation catalyzed by supported catalysts has been known for many years[171] and some interesting developments have been reported recently[53,172,173] but will not be considered further here.

Metal atom vaporization techniques have been described where metals are vaporized into frozen organic solvents. Generally, decomposition occurs when the frozen solvent–metal mixtures are warmed to room temperature. Thus, the metal atom techniques have mostly been used as an alternative method for generating supported catalysts.[174,104]

Reports of hydrogenations employing unsupported catalysts date back to the early part of this century.[175] The six platinum group metals (Ru, Os, Rh, Ir, Pd, and Pt) have been investigated as unsupported catalysts.[176] Alcohol solutions of these metals are active catalysts with varying degrees of selectivity for the deuteration of 1,2- and 1,6-dimethylcyclohexenes.

Both unsupported Pd and Pt colloids are active for selective hydrogenation of alkynes to alkenes. When Pt was employed, the double bond was in the same place as the original triple bond, while Pd catalysts caused migration of the resultant double bond. Both Pd and Pt catalyzed cis–trans isomerization of double bonds.[177]

Unsupported Ni colloids are prepared by reducing $NiBr_2$ with Zn powder. These preparations catalyze hydrogenation of styrene,[178] nitro,[179] and alkynyl[180] groups. Unsupported Ni colloids also catalyze disproportionation of deuterated 1,4-cyclohexadiene.[181] Unsupported iron colloids can be prepared by thermal decomposition of $Fe(CO)_x$ and (organo)$Fe(CO)_x$ precursors, and they catalyze hydrogenation of olefins.[67]

Ionizing radiation reduces solutions of chloroplatinic acid to give 35-Å Pt particles. Under irradiation conditions, these mixtures catalyze hydrogenation of nitrobenzene to aniline.[72]

Colloidal mixtures of both Ir and IrO_2 have been reported. Colloidal Ir was a good catalyst for hydrogenation of nitrobenzene to aniline, whereas colloidal IrO_2 did not catalyze this reaction.[182]

Stable, unprotected colloids of Ni_2B were prepared by reduction of $NiCl_2$ with $NaBH_4$. The colloids were active catalysts for hydrogenation of ketones, aldehydes, and carbon–carbon double bonds.[65,68]

Protected or Stabilized Colloids

A variety of the common polymers has been used to stabilize metal colloids. However, many protected colloids failed to show reproducible activity as catalysts.[75] Initial success was reported for the use of synthetic polymers (mostly PVA) to stabilize palladium and platinum colloids used as hydrogenation catalysts.[61,183] Several reports have recently focused on the preparation of soluble, polymer-protected colloids and their use as hydrogenation catalysts, for example, reduction of $RhCl_3$ in alcohol in the presence of PVP-generated colloids of different particle size, depending on the reaction conditions. As shown in Table 10, PVP-protected Rh colloids were active catalysts for hydrogenation of unsaturated groups. The activity generally improved with smaller particle size.[75]

Several reports describe the use of polymer-protected colloids as catalysts for hydrogenations (Table 11).[187]

The Pd colloid, stabilized by PVP, was highly selective as a hydrogenation catalyst. In the hydrogenation of 1,5-cyclooctadiene, the cyclooctene product was produced with over 99% selectivity (vs cyclooctane).[70,82] The analogous PVP-stabilized Rh colloid was a catalyst for hydrogenation of 1,5-cyclooctadiene, but in this case cyclooctane was the only observed product.[82]

Table 10. Catalytic Activity of Polyvinylpyrrolidone-Protected Rhodium Colloids for Hydrogenation of Olefins and Diolefins (Reprinted from Ref 75; Copyright 1985 Hüthig and Wepf Verlag, Basel.)

	catalytic activity (H_2 mol/Rh g-atom·s)[a]		
substrate	Rh-PVP-MeOH/H_2O, 34 Å[b]	Rh-PVP-EtOH, 22 Å[b]	Rh-PVP-MeOH/NaOH, 9 Å[b]
1-hexene	15.8	14.5	16.9
cyclohexene	5.5	10.3	19.2
2-hexene	4.1	9.5	12.8
styrene	1.9	2.5	3.2
methyl vinyl ketone	3.7	4.3	7.9
mesityl oxide	0.6	4.7	31.5
methyl acrylate	11.2	17.7	20.7
methyl methacrylate	5.8	15.1	27.6
acrylonitrile	0.5	0.8	0.9
cyclooctene	0.6	1.1	1.2
1,3-cyclooctadiene	3.7	9.8	17.5
1,5-cyclooctadiene	2.6	3.7	3.7
1-hexyne	0.1	0.1	0.2

[a] Hydrogenation conditions: 30 °C; total pressure, 1 atm; [Rh] = 0.01 mM; [Substrate] = 25 mM; solvent, methanol (20 mL). [b] Average diameter of rhodium particles.

Table 11. Polymer-Protected Colloids as Hydrogenation Catalysts

substrate(s)	metal(s)	polymer	reference
1,3-cyclooctadiene	Pd	PVP	184
Methyl linoleate, soybean oil	Pd	PVP	185
cyclohexene	Rh, Pd, Os, Pt	PVA, PVP, PMVE	63
cyclohexene	Rh	PVA	62
hexadienes	Pd	PVP	80
cyclooctadienes	Pd	PVP	185b
alkynes	Pd	PEG	186

An alternative to polymers as colloid protecting groups are surfactants. Water-soluble colloids of platinum were prepared with cationic and anionic surfactants, dodecyltrimethylammonium chloride and sodium dodecyl sulfate, respectively. The reduction of chloroplatinic acid was achieved with either irradiation or hydrogen. Both methods produced stable, surfactant-protected colloids.[94] These platinum colloids were active catalysts for the hydrogenation of vinyl acetate.

Several reports describe the surfactant- and/or polymer-stabilized colloids and their use as hydrogenation catalysts in biphasic media. Control of the interfacial tension between the aqueous and organic layers leads to improved catalytic systems.[188] Water-soluble surfactants permit preparation of 20 Å diameter Rh colloids. The Rh colloidal mixtures were used as catalysts for hydrogenation of liquid alkenes in a purely biphasic system without added solvent. Details of the colloids and their catalytic activities are shown in Table 12, where CMC is critical micellar concentration and CFC is critical flocculation temperature, surfactant = $RC[C_6H_4SO_3Na]_3$.[189] Other surfactant work has also appeared.[85,181,190]

Metal colloids have been prepared within polymerized vesicles or micelles which themselves are colloidal suspensions. A dispersion of dipalmitoylphosphatidylcholine (DPPC) and $C_{16}H_{33}(H_2C{=}CHC_6H_4\text{-}NHCO(CH_2)_{10})(CH_3)_2N^+Br^-$ formed an aqueous vesicle after sonication. Addition of K_2PtCl_4 to the solution followed by UV irradiation yielded a colloid within the vesicle. The platinum vesicle was a catalyst for hydrogenation of ethylene under a variety of conditions.[191] Other reports of catalytic activity of metallic colloids within vesicles include other platinum/palladium examples[99,95] and those that contained colloidal Ni_2B, Co_2B, and NiCoB.[192,193] Several studies employ polymeric materials in conjunction with colloids where the polymer is not soluble in the reaction medium. These systems, therefore, do not fall within the scope of this review. However, the concepts are related to those described above where the additional feature is the presence of a cross-link in the polymer protecting group rendering it insoluble.[76–79,83,86,194,195] An unusual case is the stabilization of rhodium colloids with cyclodextrins. Cyclodextrins generally are used to microencapsulate molecular compounds.[196] The Rh colloid–cyclodextrin complex was insoluble in aqueous solution. However, the suspension was active as a catalyst for hydrogenation of olefins.[197]

Mixed-metal catalytic systems provide the opportunity to achieve synergy between the metals. In one system a mixed colloid of Pt and Cd was prepared and its catalytic activity for hydrogenation of crotonalde-

Table 12. Characteristics of Colloidal Suspensions of Rh(0) (Reprinted from Ref 189; Copyright 1991 Elsevier Sequoia S. A.)

		Rh(0) colloidal suspensions[a]			hydrogenation of 1-octene[m]		
					turnover number (mol product/mol Rh·h)[a]		remaining activity during the second run (%)
stabilizer	CMC (mol L^{-1})	[1] (mol L^{-1})	N[c]	particle size[b] (Å)	first run	second run	
1a ($C_{18}H_{37}$)	2×10^{-3}	1.9×10^{-2} [d]	10	2–30[g] (detection limit)	19[p]	18[p]	95
	2×10^{-3}	9.5×10^{-4} [e,f]	10	20–30[g] (detection limit)	262[q]	260[q]	99
1b ($C_{16}H_{33}$)	3.5×10^{-3}	1.9×10^{-2} [d]	10	20–30[g] (detection limit)	36[p]	28[p]	78
	3.5×10^{-3}	9.5×10^{-4} [e,h]	10	20–30[g] monodisperse	247[q]	250[q]	100
	3.5×10^{-3}	3.8×10^{-4} [e,f]	10	20–30[g] monodisperse	277[q]	275[q]	99
	3.5×10^{-3}	9.5×10^{-3} [d]	5	50[g] monodisperse	17[p]	5[p]	29
	3.5×10^{-3}	10^{-3} [e]	0.5	50–800[g] polydisperse	60[q]	11[q]	18
1c (C_9H_{19})	10^{-2}	1.9×10^{-2} [d]	10	80–600[j] polydisperse	19[p]	8[p]	42
1d [$(CH_2)_2OH$]	–	1.9×10^{-2}	10	250–1000[k] polydisperse	120[q]	5[q]	4
1e (CH_3)	–	1.9×10^{-2}	10	250–1000[l] polydisperse	39[q]	10[q]	25

[a] The colloidal suspensions were prepared by addition of 5.8×10^{-4} mol $NaBH_4$ to 150 mL of an aqueous solution of 1 (variable concentration) and $RhCl_3 \cdot 3H_2O$ (2.8×10^{-4} mol). Reduction occurred instantaneously. The aqueous suspensions were neutralized by addition of diluted HCl before characterization and catalytic use. [b] Determined by TEM. [c] Molar ratio 1/Rh. [d] Above the CMC. [e] Below the CMC. [f] This suspension was obtained by dilution (20 times) of the upper suspension. [g] Suspensions stable for months, CFT > 100 °C, no flocculation upon addition of NaCl or $MgSO_4$ until their limit of solubility. [h,i] These suspensions were obtained by dilution (*h*, 20 times; *i*, 50 times) of the above suspension. [j] Complete flocculation after 48 h, CFT = 85 °C, CFC = 2.7 mol L^{-1} ($MgSO_4$). [k] Complete flocculation after 48 h, CFT = 80 °C, CFC = 1.9 mol L^{-1} ($MgSO_4$). [l] Complete flocculation after 24 h, CFT = 65 °C, CFC = 1.7×10^{-1} mol L^{-1} (NaCl). [m] Experimental conditions: 20 mL colloidal suspension, 2 mL (1.3×10^{-2} mol) 1-octene, 25 °C, 1 atm H_2; the catalytic reactions were carried out in a standard ordinary pressure hydrogenator equipped with a magnetic stirrer. At the end of the reaction, determined by the volume of hydrogen consumed and gas chromatography control, the product (organic layer) was separated by decantation and the aqueous colloidal suspension was filtered on a 0.45-μm micropore before recycling. [n] Determined by GC analysis and hydrogen consumption. [p] The reaction mixture formed an emulsion. [q] The reaction mixture consisted of two distinct liquid phases.

hyde investigated. Only the Pt–Cd-containing colloids were able to effect hydrogenation of the C=O group, while Pt-only colloids catalyzed hydrogenation of the C=C groups.[198]

In one bimetallic colloid of Pt–Au, several members of the citrate-stabilized series $Pt_{100-x}Au_x$ ($0 < x < 100$) were prepared and analyzed by HREM (Figure 14).[109] The catalyzed rates of dehydrogenation, isomerization, and hydrogenolysis of *n*-butane were a function of Pt–Au composition.[109] Other studies employed the polymer-stabilization technique to prepare mixed metal colloids and investigate their catalytic activity. While monometallic colloids of either Pd or Pt were small, they had a tendency to agglomerate, whereas excellent uniformity of particle size was observed for PVP-stabilized Pd-Pt bimetallic colloids over a wide Pd/Pt ratio (average diameter 15 Å). PVP-stabilized Pd–Au bimetallic colloids were uniformly 34 Å in diameter, again, with no tendency to aggregate. The bimetallic Pd–Pt colloids were more active toward hydrogenation of 1,3-cyclooctadiene than either Pd or Pt alone. Likewise, the Pd–Au colloids were more active as catalysts than either metal alone.[199] Work is described for PVP-stabilized Pt-Rh,[200] Rh–Au, and Pd–Pt.[201]

Cluster Catalysis

A large impetus for cluster research in the late 1970s was as a model for metal-surface catalysts.[202,203] Therefore, it is not surprising that hundreds of studies have been published on cluster catalysis. By far the most widely studied reaction has been hydrogenation. Clusters provide low-energy pathways which lead to reactions with high selectivity to products.[202] A theoretical basis for explaining these fundamental steps has appeared.[146] Hydrogenation of olefins catalyzed by clusters of the nickel triad has been reviewed.[204] The Fischer–Tropsch reaction, catalyzed by clusters, has also received much attention.[24,205]

One area of continuing debate is whether a reaction is catalyzed by an intact cluster. One possibility is that cluster precursors decompose to mononuclear catalysts under reaction conditions. For alkene and alkyne hydrogenation reactions, a number of studies have examined whether the cluster catalyst precursor stays intact during catalysis. Hydrogenation of pinene and camphene with ruthenium dimers and trimers leads to decomposition of the catalysts, which could not be regenerated.[206] Thus, under these reaction conditions, the cluster formed unreactive bulk metal or mononuclear species.

Tetranuclear hydridocarbonylosmium clusters are catalyst precursors for the hydrogenation of styrene.[207] This work ruled out catalysis by colloidal osmium by two of the methods described above.[161,167] Furthermore, metallic osmium was generated intentionally in solution and shown to have poor catalytic activity versus that obtained starting with the cluster. However, formation of mononuclear species cannot be precluded, because the kinetic data do support fragmentation of the osmium tetramer.

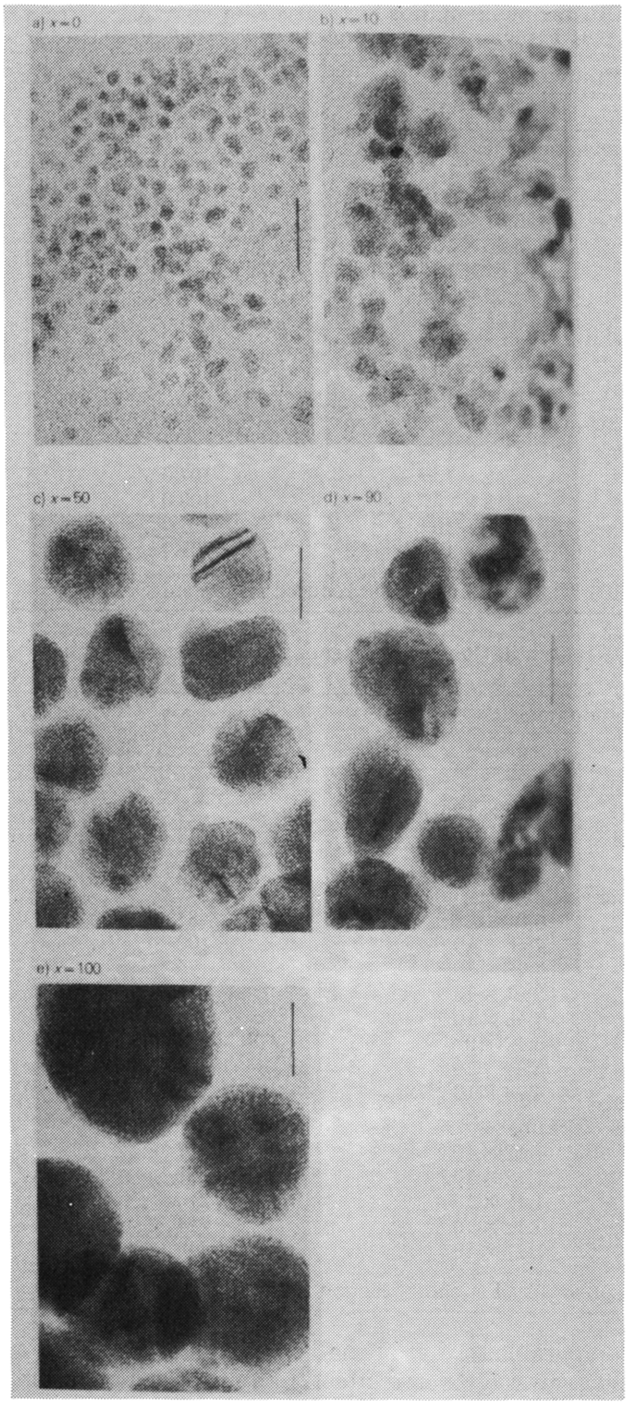
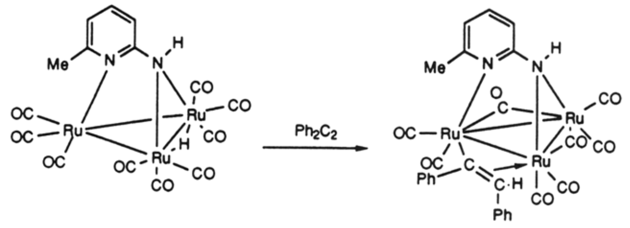


Figure 14. HREM of colloidal bimetallic compositions $Pt_{100-x}Au_x$: (A) $x = 0$, (B) $x = 10$, (C) $x = 50$, (D) $x = 90$, (E) $x = 100$. Scale line = 10 nm. (Reprinted from ref 108; copyright 1987 VCH Verlagsgesellschaft mbH.)

A series of reports describes olefin hydrogenation by palladium carbonyl acetate tetramer.[208-210] While these reports do not specifically address the nuclearity of the catalyst, a variety of higher and lower nuclearity Pd clusters form under the following reaction conditions (eq 2).[208]

$$Pd_4(CO)_4(OAc)_4 + 2H_2 \rightarrow {}^4/_x Pd_x + 4CO + 4AcOH \quad (2)$$

However, if phen was present, formation of bulk metal was prevented (eq 3).[209]



1

2

Figure 15. Active Ru_3 catalyst for hydrogenation of alkynes to alkenes. (Reprinted from ref 227; copyright 1992 Elsevier Sequoia S. A.)

$$[Pd_4phen_4(CO)_4][(OAc)_4] \xrightarrow{H_2} [Pd_2phen_2(CO)(H)][OAc]\cdot HOAc \quad (3)$$

Catalytic conversion of alkynes to alkenes has been reported with the rhodium hydride dimer $[(\mu\text{-H})Rh(P(O\text{-}iC_3H_7)_3)_2]_2$. Under reaction conditions, alkynes were converted to *trans*-alkenes and a mononuclear compound. The mononuclear compound in turn catalyzed hydrogenation of alkynes to *cis*-alkenes.[211] These results were reminiscent of work published[212] from the thesis[213] of the author of this review. In another study, the dimer $Cp_2V_2(CO)_5$ was a catalyst precursor for the hydrogenation of diphenylacetylene to *cis*-stilbene under photochemical conditions. None of the available $CpV(CO)_x(alkyne)_y$ mononuclear species displayed the activity found for the dimeric precursor. The lack of activity of the monomers and observation of a dimeric intermediate in solution suggested catalysis via a dimer.

Other studies have concluded that catalysis occurs via an intact cluster on the basis of chemistry observed which does not take place via mononuclear metal species. Various tri- and tetranuclear osmium clusters catalyze hydrogenation of cyclohexene. Catalysis via clusters was suggested.[214] Another study proposed catalysis via clusters on the basis of kinetic data and other indirect evidence.[215] Yet another indirect way that suggests catalysis via intact clusters is the observation of catalysis via mixed-metal clusters that differs for that observed for either mononuclear compounds of the individual metals.[216]

One of the earliest and convincing examples of catalysis by a cluster was olefin hydrogenation employing $[CpFeCO]_4$.[217] The evidence that supported catalysis via the iron tetramer included the fact that the tetramer was recovered in high yield after each catalysis run. In addition, the most likely monomer catalyst candidate is $CpFe(CO)_2H$, which forms from $[CpFe(CO)_2]_2$ under an atmosphere of hydrogen. The dimer was not catalytically active and the tetramer did not form from reaction of $[CpFe(CO)_2]_2$ and hydrogen. Several other studies contain data which supports catalysis of olefin hydrogenation via intact clusters.[218-226]

Some approaches attempt to prevent cluster degradation under catalytic conditions by employing robust bridging ligands. One example is the complex $Ru_3(\mu\text{-H})(\mu_3\text{ampy})(CO)_9$, where ampy = 2-amino-6-methylpyridine. The ruthenium trimer was a catalyst precursor for hydrogenation of alkenes and alkynes. The proposed active catalyst is shown in Figure 15[227] and was observed under catalytic conditions by IR. A second approach to prevent formation of mononuclear species during catalyzed hydrogenation was the use of carborane frameworks to maintain cluster integrity.[228,229] (See

Table 13. Cluster and Substrate Concentration and Substrate/Cluster Molar Ratios in Hydrogenation and Isomerization Experiments (Reprinted from Ref 231; Copyright 1991 Elsevier Sequoia S. A.)

		concentration (mol/L)		
experiments[a]	cluster	cluster	substrate	substrate/cluster molar ratio
Hydrogenation of Diphenylacetylene				
A	$Fe_3(CO)_{10}(P^iPr)(\mathbf{1})$[b]	1.05×10^{-5}	5.69×10^{-4}	54.2
B	$Fe_3(CO)_{10}[P(NEt_2)](\mathbf{1a})$	1.04×10^{-5}	6.98×10^{-4}	67.1
C	$H_2Fe_3(CO)_9(P\text{-}p\text{-tolyl})(\mathbf{2})$[d]	9.24×10^{-6}	5.61×10^{-4}	60.7
D	$H_2Fe_3(CO)_9(P\text{-}p\text{-tolyl})$[b]	1.01×10^{-5}	5.65×10^{-4}	55.9
E	$Fe_3(CO)_9(P^iBu)_2(\mathbf{3})$	9.78×10^{-6}	5.61×10^{-4}	57.4
F	$Fe_3(CO)_9(NEt)_2(\mathbf{3a})$	1.19×10^{-5}	5.69×10^{-4}	47.8
G	$Ru_4(CO)_{13}(PPh)(\mathbf{4})$[d]	2.28×10^{-6}	5.65×10^{-4}	24.8
H	$Ru_4(CO)_{13}(PPh)$	7.42×10^{-6}	5.61×10^{-4}	75.6
K	$Ru_4(CO)_{13}(PPh)$	7.22×10^{-6}	5.85×10^{-4}	81.0
J	$Ru_4(CO)_{13}(PPh)$[e]	2.28×10^{-6}	5.64×10^{-4}	247.0
Isomerization of *cis*-Stilbene				
I	$Fe_3(CO)_{10}(PiPr)(1)$	1.00×10^{-5}	1.12×10^{-3}	112.0
L	$Fe_3(CO)_{10}(PiPr)$	1.05×10^{-5}	1.12×10^{-3}	107.0
M	$H_2Fe_3(CO)_9(P\text{-}p\text{-tolyl})(2)$	1.12×10^{-5}	1.12×10^{-3}	100.0
N	$Ru_4(CO)_{13}(PPh)(4)$	7.42×10^{-6}	1.12×10^{-3}	151.0
O	$Ru_4(CO)_{13}(PPh)$	2.28×10^{-6}	1.12×10^{-3}	491.0

[a] The letters indicate the experiment. [b] At 120 °C. [c] At 80 °C. [d] At 100 °C. [e] At 120 °C under reduced H_2 pressure.

Table 14. Cluster and Substrate Concentrations and Substrate/Cluster Ratios in Hydrogenation and Isomerization (Reprinted from Ref 232; Copyright 1989 Elsevier Sequoia S. A.)

		concentration (mol/L)		
experiment[a]	cluster	cluster	substrate	substrate/cluster molar ratio
Hydrogenation of Hex-3-yne				
(A)	$HRu_3(CO)_9(PPh_2)$	7.65×10^{-6}	1.76×10^{-3}	230
(B)	$HRu_3(CO)_7(PPh_2)_3$	5.15×10^{-6}	1.76×10^{-3}	342
(C)	$HRu_3(CO)_7(PPh_2)_3$[b]	5.15×10^{-6}	1.76×10^{-3}	342
Hydrogenation of Diphenylacetylene				
(D)	$HRu_3(CO)_{10}(PPh_2)$	7.15×10^{-6}	6.0×10^{-4}	84
(E)	$HRu_3(CO)_9(PPh_2)$	7.42×10^{-6}	7.46×10^{-4}	100
(F)	$HRu_3(CO)_9(PPh_2)$[c]	7.86×10^{-6}	7.46×10^{-4}	95
(G)	$HRu_3(CO)_7(PPh_2)_3$	6.0×10^{-6}	2.81×10^{-4}	47
(H)	$HRu_3(CO)_7(PPh_2)_3$	4.90×10^{-6}	7.46×10^{-4}	152
(I)	$HRu_3(CO)_7(PPh_2)_3$[b]	5.92×10^{-6}	6.4×10^{-4}	108
(K)	$Ru_3(CO)_{10}(PPh_2H)_2$	6.28×10^{-6}	5.84×10^{-4}	93
(L)	$Ru_3(CO)_9(PPh_2H)_3$	4.19×10^{-6}	4.78×10^{-4}	138
Isomerization of *cis*-Stilbene[d]				
(M)	$HRu_3(CO)_{10}(PPh_2)$	7.15×10^{-6}	1.12×10^{-3}	157
(N)	$HRu_3(CO)_9(PPh_2)$	7.42×10^{-6}	1.12×10^{-3}	151
(O)	$HRu_3(CO)_7(PPh_2)_3$	5.21×10^{-6}	1.12×10^{-3}	215
(P)	$Ru_3(CO)_{10}(PPh_2H)_2$	5.23×10^{-6}	1.12×10^{-3}	214
(Q)	$Ru_3(CO)_9(PPh_2H)_3$	4.49×10^{-6}	1.12×10^{-3}	249

[a] The letters indicate the experiment. [b] Under decreasing hydrogen pressure. [c] For short reaction times. [d] Without hydrogen.

Figure 27.) A third approach used chelating, optically active phosphines on a Rh_6 cluster. Asymmetric reduction of prochiral olefins was achieved using this rhodium cluster. Results with $Rh_6(CO)_{10}[(-)DIOP]_3$ contrasted those obtained with mononuclear catalysts.[230]

A large number of ruthenium and iron carbonyl phosphine clusters have been used as hydrogenation catalysts (Tables 13[231] and 14).[232] Extensive work has suggested cluster catalysis for these and related classes of compounds.[16,233-235]

The mixed-metal Pt–M (M = Co, Fe, Mo) clusters were investigated as catalysts for hydrogenation of olefins, diolefins, and internal acetylenes.[236,237] The catalyst with a $PtMo_2$ framework was completely recovered after a catalytic run. On the other hand, the catalyst based on a Pt_2Co_2 framework extensively rearranges under catalytic conditions. One product of the rearrangement of the Pt_2Co_2 cluster was a Pt_5 cluster. The catalytic activity of the Pt_5 cluster was comparable to that of the Pt_2Co_2 cluster, and the Pt_5 cluster was recovered intact from a hydrogenation run. Reactions catalyzed by the Pt–M clusters formed colloids as determined by filtration of the reaction solution through cellulose,[161] but these colloids had poor catalytic activity compared with the clusters.

A rather detailed analysis has been reported on the catalytic species present in solutions where olefins were hydrogenated in the presence of iridium–polyoxoanion clusters.[238] The presence of Ir(0) "colloids" (bare metal clusters) was ruled out. Solutions where catalysis had occurred (18 000 turnovers of hydrogenation of cyclohexene) could be evaporated to dryness, redissolved, and then shown to retain their catalytic activity. These authors believe no known colloid is able to survive such treatment, so they concluded that the Ir-supported polyoxoanion cluster must have remained intact during catalysis. However, Pt with water-soluble PVP stabilizer does indeed survive such treatment as described above.[111a,b]

Table 15. Conversion of CO–H_2 to Ethylene Glycol: Reaction Sequences Observed by High-Pressure IR Spectroscopy (Reprinted from Ref 203; Copyright 1982 the Royal Society of Chemistry.)

catalyst precursors	species present at 90 MPa and 473 K
$Rh(CO)_2acac \xrightarrow{\text{no base}} Rh_6(CO)_{16}$	$Rh_6(CO)_{16} + [Rh_5(CO)_{15}]^-$ (tr.)
$Rh(CO)_2acac \xrightarrow{\text{2-OHpy}} [Rh_5(CO)_{15}]^-$	$[Rh_5(CO)_{15}]^-$
$[Rh_{12}(CO)_{30}]^{2-} \xrightarrow{\text{no base}} [Rh_5(CO)_{15}]^- + Rh_4(CO)_{12}$	$[Rh_5(CO)_{15}]^- + Rh_6(CO)_{16}$
$[Rh_{12}(CO)_{30}]^{2-} \overset{H_2}{\rightleftharpoons} [HRh_6(CO)_{15}]^- \xrightarrow{CO-H_2} [Rh_5(CO)_{15}]^-$	
$[Rh_{12}(CO)_{30}]^{2-} \xrightarrow{\text{2-OHpy}} [Rh_5(CO)_{15}]^-$	$[Rh_5(CO)_{15}]^-$
$[Rh_6(CO)_{15}]^{2-} \rightleftharpoons [Rh_5(CO)_{15}]^- + [Rh(CO)_4]^-$	$[Rh_5(CO)_{15}]^- + [Rh(CO)_4]^-$
$Ir(CO)_2acac \xrightarrow{\text{2-OHpy}} Ir_4(CO)_{12}$	$Ir_4(CO)_{12}$

$[Rh_{13}(CO)_{24}H_3]^{2-}$ also observed, but only under CO-deficient conditions

A mixed metal Pt–Ir cluster was an active catalyst for hydrogenation of olefins.[165] The presence of large clusters or colloids following catalysis was ruled out by the absence of light scattering and by filtration of catalyst solutions through micropore filters. Resultant solutions retained their catalytic activity. Catalysis by intact clusters was suggested because spectroscopic analysis showed only the starting cluster during all phases of a catalytic run.

Hydrogenation of Other Functional Groups

Clusters have been employed as catalysts for reactions related to olefin/alkyne hydrogenation. Several reviews[203,239,240] summarize the in situ studies that established the presence of metal carbonyl cluster catalysts in the CO–H_2 to ethylene glycol reaction (Table 15).[203]

The cluster $Rh_6(CO)_{16}$ was a catalyst precursor for the reduction of benzaldehyde to benzyl alcohol in the presence of H_2 and CO using $NaHCO_3$ as the base and MeOH as the solvent.[241] In situ IR studies were consistent with the clusters $Rh_{12}(CO)_{30}^{2-}$ and $Rh_5(CO)_{15}^-$, whose presence was anticipated by the reactions in Figure 16, which also suggested formation of $Rh(CO)_4^-$. A detailed kinetic analysis of the reaction showed a small $\Delta S^{\ddagger}$, which can be ascribed to the fact that breaking one metal–metal bond in a large cluster (e.g. $Rh_6(CO)_{15}^{2-}$), has a minimal effect on structural rigidity. The kinetic analysis argued against catalysis via a mononuclear species because of the low ΔS, a dependency on base, a zero-order dependence on benzaldehyde, and a negative dependence on CO concentration. Formation of the imputed mononuclear $Rh(CO)_4^{-1}$ would be favored by *high* CO pressures.

Glycol was produced from the reaction of CO and H_2 in the presence of $Co_2(CO)_8$ under forcing conditions. Improved activity for production of glycol was achieved by adding both $P(iPr)_3$ and $Ru_3(CO)_{12}$. Direct IR measurements taken at 20 atm identified $Co_2(CO)_8$, $Ru(CO)_4[(iPr)_3P]$, and $Ru(CO)_5$, but did not detect a mixed-metal carbonyl cluster.[242]

Ru carbonyl clusters were described above as catalysts for hydrogenation of olefins/alkynes. They are also catalysts for transfer hydrogenation of α,β-unsaturated aldehydes (2-propanol is the hydrogen donor).[243,244] These clusters are unusually selective toward preferential reduction of the aldehydic functionality. A proposed mechanism for the reaction is shown in Figure 17, where catalysis occurred via intact clusters. Isotope exchange studies were inconsistent with behavior previously noted for mononuclear species. In addition, a first-order dependence on the cluster argues against breakdown to clusters of lower nuclearities.

$$Rh_6(CO)_{16} + 2\,OH^- \rightarrow Rh_6(CO)_{15}{}^{2-}\ [\text{Green}] + H_2O + CO_2$$

$$2Rh_6(CO)_{15}{}^{2-} \xrightarrow{O_2} Rh_{12}(CO)_{30}{}^{2-}$$

$$Rh_{12}(CO)_{30}{}^{2-} + Rh_6(CO)_{15}{}^{2-} \overset{CO}{\rightleftharpoons} Rh_5(CO)_{15}{}^-$$

$$Rh_6(CO)_{15}{}^{2-} + 4\,CO \rightleftharpoons Rh_5(CO)_{15}{}^- + Rh(CO)_4{}^-$$

Figure 16. Cluster reactions relevant to the Rh-cluster-catalyzed reduction of benzaldehyde to benzyl alcohol. (Reprinted from ref 241; copyright 1982 Elsevier Sequoia S. A.)

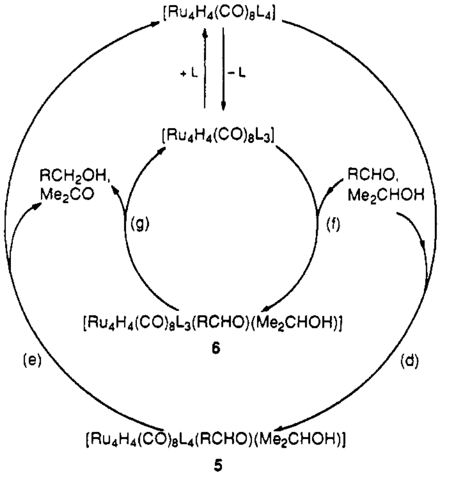


Figure 17. Proposed mechanism for the Ru-cluster-catalyzed reduction of aldehydes. Kinetic data suggests **5** and **6** are short-lived intermediates and that cluster breakdown to lower nuclearity species is ruled out. (Reprinted from ref 243; copyright 1992 the Royal Society of Chemistry.)

Similar behavior reported for the Ru clusters was found for osmium clusters. Data suggested catalysis

Table 16. Homologation of Methanol Catalyzed by Mixed Transition Metal Cluster[a] (Reprinted from Ref 260; Copyright 1981 the Chemical Society of Japan.)

		yield (%)[b]					selectivity (%)[c]	
catalyst	conversion (%)	AcH	DMA[d]	EtOH	AcOMe	Me_2O	total C_2	EtOH
$[Co_2(CO)_8]$[e]	46	3.9	25	0.7	2.5	22	31	1.4
$[Co_4(CO)_{12}]$[f]	48	4.0	29	0.6	2.8	23	32	1.2
$[(dpe)PdCo_2(CO)_7]$,[e] **1**	61	10	30	0.8	5.9	18	39	1.3
$[(dpe)PtCo_2(CO)_7]$,[e] **2**	49	6.0	24	1.6	3.7	19	36	3.3
$[RhCo_3(CO)_{12}]$	52	6.0	27	0.8	8.4	16	39	1.6
$Na[RuCo_3(CO)_{12}]$, **3**	46	1.3	5.6	16	4.4	20	41	30
$Cs[RuCo_3(CO)_{12}]$, **4**	43	0.7	2.6	18	5.6	16	51	41
$[Et_4N][RuCo_3(CO)_{12}]$, **5**	41	0.5	1.7	21	0.4	15	54	51
$[Et_4N][Ru_3Co(CO)_{13}]$,[f] **6**	40	0	0.4	9.1	2.6	27	26	23
$[Ru_3(CO)_{12}]$	18	0	0	2.8	0.7	31	11	10

[a] Unless otherwise noted, the catalyst (0.13 mmol), methanol (500 mmol), CH_3I (5 mmol), and benzene (10 mmol) as internal standard were charged in a 200-mL stainless steel autoclave lined with titanium. Carbon monoxide (40 kg/cm^2) and hydrogen (80 kg/cm^2) were then introduced and the mixture was stirred for 3 h at 180 °C. [b] The yield was calculated (CH_3OH consumed for product)/(CH_3OH charged) × 100. [c] The selectivity was obtained by [product (mmol)/CH_3OH reacted (mmol)] × 100. [d] DMA is acetaldehyde dimethyl acetal. [e] The amount of the catalyst used was 0.2 mmol. [f] The amount of the catalyst employed was 0.1 mmol.

via an osmium carbonyl phosphine cluster in the hydrogenation of a variety of α,β-unsaturated aldehydes.[245] Another ruthenium cluster, $[H_3Ru_4(CO)_{12}]^-$, catalyzed hydrogenation of the β-keto functional group in acetocetic amides and esters. The proposed mechanism included the intact cluster.[246] Yet another ruthenium cluster catalyzed the transfer hydrogenation and disproportionation of cyclohex-2-en-1-one. In this case, cluster carbonyl complexes were observed in situ and isolated at the end of a catalytic run. The clusters initiate free radicals, which in turn leads to the observed reactions.[247]

Hydrogenation of CO

The hydrogenation of CO, which leads to oxygenate products, has been extensively studied due in part to its many industrial applications. Two excellent reviews describe the cluster precursors which catalyze this reaction.[248,249] One study showed that a variety of ruthenium clusters, $H_4Ru_4(CO)_{12}$, $[H_3Ru_4(CO)_{12}]^-$, $Ru_3(CO)_{12}$, and $[Ru_6C(CO)_{16}]^{2-}$, had similar activities for the CO/H_2 reaction at 1300 atm, 225–275 °C. The clusters all yielded a common, soluble ruthenium compound, $Ru(CO)_5$. Kinetic investigations supported catalysis via a mononuclear species for methanol formation. However, hydrocarbon formation appeared to be due to metallic ruthenium.[157] Earlier work also implicated mononuclear catalytic species beginning from Ru clusters.[250–252]

Carbon monoxide was hydrogenated in the presence of $Os_3(CO)_{12}$ and BBr_3.[253] In this case more mild conditions, 2 atm, 180 °C, were employed than for the Ru system described above. Also in contrast to the Ru system, hydrocarbon products were produced, but all data suggested catalysis via soluble, intact clusters. The proposed catalyst was $Os_2(CO)_4Br_4$, which was recovered quantitatively after a catalytic run. Catalytic experiments using osmium metal led to different reaction rates and product distributions than those obtained with soluble clusters.

Hydrogenation of quinolines and isoquinolines was achieved using $Rh_6(CO)_{16}$ as a catalyst precursor under water–gas shift conditions. The exact nature of the catalytic species was not known, but the proposed active catalyst was a cluster containing ≥2 Rh atoms, CO, and an N-bound quinoline.[254]

Table 17. Current Processes for Methyl Formate Production (Reprinted from Ref 263; Copyright 1987 Elsevier Sequoia S. A.)

reactants	catalyst	phase(s)	temp (°C)	pressure (atm)	ref
2MeOH	CuZnZr	gas–solid	285	1	14
$MeOH/O_2$	$SnO_2–MoO_3$	gas–solid	160	na[a]	17
CO_2/H_2	$Ru(acac)_3$	liquid	250	1300	19
CO_2/H_2	$PPN[\mu\text{-}HW_2(CO_{10}]$	liquid	125	52	25a
MeOH/CO	NaOMe	liquid	80	45	28

[a] Operating pressure not disclosed.

CO Activation

Activation of carbon monoxide by transition metal clusters is well-documented[255–258] and is relevant to both the Fischer–Tropsch reaction and to hydroformylation (see the next section).

Metal carbonyl clusters catalyze the so-called homologation reaction of methanol (eq 4). Clusters also

$$CH_3OH + CO + 2H_2 \xrightarrow{\text{catalyst}} CH_3CH_2OH + H_2O \quad (4)$$

catalyze carbonylation of methanol to give acetic acid, methyl acetate, and dimethyl ether. Active clusters include $[FeCo_3(CO)_{12}]^-$ and $[FeCo_3(CO)_{11}PPh_3]^-$.[259] Other mixed-metal cobalt cluster carbonyl complexes catalyze the reaction in eq 4 with high efficiency. The cluster $[(dpe)MCo_2(CO)_7]$ (dpe = $Ph_2PCH_2CH_2PPh_2$, M = Pd, Pt) was prepared from $Na[Co(CO)_4]$ and $dpeMCl_2$. The ruthenium–cobalt mixed metal clusters $[M']^+[RuCo_3(CO)_{12}]$ (M′ = Cs, Et_4N) were prepared from $Na[Co(CO)_4]$ and $RuCl_3$. Some typical results are shown in Table 16. The selectivity for ethanol was highest for the Ru–Co cluster, while the overall percent conversion was highest for the Pd–Co cluster.[260] The Ru–Co mixed-metal system has been examined in more detail.[261] Another cluster which catalyzes conversion of synthesis gas to methanol is $[(OAc)_2PtPPh_3]_2$.[262]

The importance of methyl formate as a feedstock has been discussed with the current methods of production shown in Table 17.[263] The most common method of production was based on the base-catalyzed carbonylation of methanol (last line of Table 17). Several metal carbonyl monomers and dimers catalyze formation of alkyl formates from CO and alcohol (Table

Table 18. Formation of Alkyl Formate from Carbon Monoxide and Alcohol Using Group VIB Metal Carbonyls[a] (Reprinted from Ref 263; Copyright 1987 Elsevier Sequoia S. A.)

run no.	catalyst[b]	time (h)	ROH	HCO_2R (mmol)	turnover[c]
1	$Et_4N[HW_2(CO)_{10}]$	24	MeOH	36	269
2	$Et_4N[HW_2(CO)_{10}]$	12	MeOH	37	248
3	$K[HW_2(CO)_{10}]$	24	MeOH	36	246
4	$[Na\cdot crypt][W(CO)_5O_2CH]$[d]	24	MeOH	29	185
5	$PPN[CH_3W(CO)_5]$[e]	24	MeOH	43	305
6	$W(CO)_6$/KOMe	24	MeOH	47	333
7	KOMe	24	MeOH	7	50
8	$W(CO)_6$	24	MeOH		
9	$Bu_4N[HCr_2(CO)_{10}]$	24	MeOH	32	219
10	$K[HW_2(CO)_{10}]$	24	EtOH	8	55
11	$Bu_4N[HW_2(CO)_{10}]$	24	*m*-cresol		

[a] Temperature, 125 °C; P_{CO} = 250 psi; 15 mL of alcohol solvent. [b] Catalyst concentrations were all 1.0×10^{-2} M. [c] Turnover = mol HCO_2Me/mol catalyst. [d] This species decarboxylates under the reaction conditions to afford $HW(CO)_5^-$ and CO_2. [e] This species has been shown to react quantitatively with methanol to provide $W(CO)_5OMe^-$, with subsequent production of μ-$H[W(CO)_5]_2^-$, and methane. [f] Molar ratio unity.

18). However, the mechanism probably involves mononuclear intermediates. For example, $HW_2(CO)_{10}^-$ forms $HW(CO)_5^-$ and $W(CO)_6$ under reaction conditions.[263]

Carbonylation of nitro compounds is important because it is a method to synthesize isocyanates[264] and carbamates[265] (eqs 5 and 6). On an industrial scale, supported metal oxide catalysts are often employed.[266]

$$RNO_2 + 3CO \xrightarrow{\text{catalyst}} RNCO + 2CO_2 \qquad (5)$$

$$RNO_2 + 3CO + R'OH \xrightarrow{\text{catalyst}} RNHCO_2R' + 2CO_2 \qquad (6)$$

Metal clusters $[MRh_4(CO)_{15}]^{2-}$ (M = Fe, Ru and Os) were active and selective catalysts for carbonylation of nitrobenzene in the presence of methanol to give methyl phenylcarbamate (Table 19).[265] Again, while Table 19 lists many cluster precatalysts, mechanistic studies suggest that the catalytic intermediate is $[Rh(CO)_4]^-$.

The carbonylation of nitrobenzene was also studied in the presence of $Ru_3(CO)_{12}$ and related systems as catalyst precursors. Both $Ru_3(CO)_{12}$ and $[HRu_3(CO)_{11}]^-$ were highly selective for formation of methyl phenylcarbamate (95%) with a low yield of aniline (5%) formed. Higher overall yields were achieved in acetonitrile vs *n*-octane. A mechanism based on cluster intermediates was proposed.[266] The crystal structure was solved for a cluster intermediate formed under conditions similar to those in eq 5 using methanol and $Ru_3(CO)_{12}$. The intermediate was $Ru_3(CO)_{10}(PhNCHO)$ (Figure 18).[267]

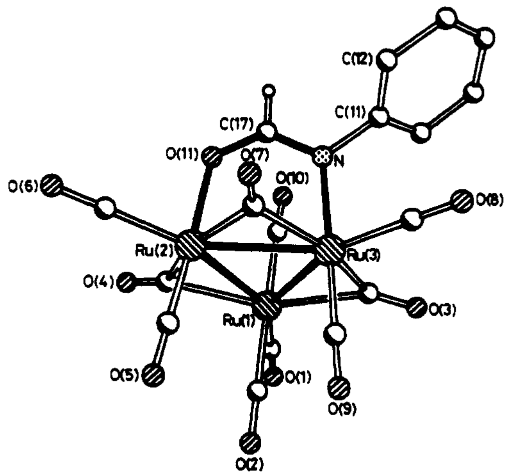


Figure 18. Three-dimensional structure of the intermediate from the reaction of $Ru_3(CO)_{12}$ with OH^-, $PhNO_2$, and CO. (Reprinted from ref 267; copyright 1989 the Royal Society of Chemistry.)

Mixed-metal clusters have also been employed for the synthesis of ethylene glycol and its monoalkyl ether derivatives. In one case a low-melting quaternary phosphonium salt was used as a medium to dissolve a mixed catalyst composed of $Ru(acac)_3$ and $Rh(acac)_3$. The melt-catalyzed conversion of synthesis gas (CO/H_2) to ethylene glycol along with its methyl and ethyl ethers. Both methanol and ethanol were formed as well. Product yields and selectivities were a function of the quaternary phosphonium salt employed.[268]

The $Rh_6(CO)_{16}$ cluster catalyzed the conversion of nonsubstituted acetylenes to furan-2(5*H*)-ones in dioxane in the presence of triethylamine, water, and carbon monoxide.[269] A closely related system catalyzes the carbonylation of olefins in the presence of N-alkylated diamines, carbon monoxide, and water.[270]

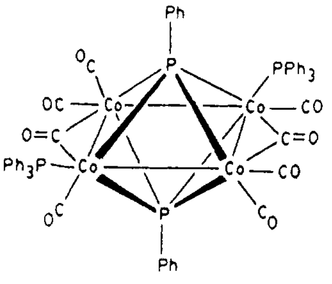
Hydroformylation

The hydroformylation reaction, eq 7, has many examples of catalysis with clusters. The large industrial

Table 19. Catalysis by Mixed-Metal Clusters[a] (Reprinted from Ref 265; Copyright 1992 Elsevier Sequoia S. A.)

catalyst	$PhNO_2$/catalyst[b]	Bipy/catalyst[b]	MeOH (mL)	conversion (%)	selectivity (%)[c]		
					carbamate	aniline	azoxybenzene
$[PPN]_2[RuRh_4(CO)_{15}]$	400	0	1.4	66.3	82.7	12.7	0
$[PPN]_2[RuRh_4(CO)_{15}]$	400	0[d]	1.4	73.1	91.1	7.2	0
$[PPN]_2[RuRh_4(CO)_{15}]$	400	8	1.4	98.5	87.9	7.5	0
$[PPN]_2[OsRh_4(CO)_{15}]$	400	8	1.4	100	89.0	9.0	0
$[PPN]_2[RuRh_4(CO)_{15}]$	400	8	0	20.6	*f*	16.0	0
$[PPN]_2[FeRh_4(CO)_{15}]$	1500	8	3	44.2	42.2	17.3	19.1
$[PPN]_2[RuRh_4(CO)_{15}]$	1500	8	3	45.5	56.6	13.8	13.5
$[PPN]_2[OsRh_4(CO)_{15}]$	1500	8	3	45.8	49.1	13.6	18.3
$[PPN][Rh_5(CO)_{15}]$	1500	8	3	51.1	58.9	13.0	13.1
$[PPN][Rh(CO)_4]$[e]	300	8/5	3	56.2	61.1	11.9	18.7

[a] Cluster = 0.025 mmol, THF = 8 mL, 60 atm, 170 °C, 1.5 h. [b] Molar ratio. [c] Calculated with respect to the consumed $PhNO_2$. [d] $Et_4N^+Cl^-$ (8/1 molar amount with respect to the cluster) was used as cocatalyst. [e] $[PPN][Rh(CO)_4]$ = 0.125 mmol. [f] Phenyl isocyanate (27.5% selectivity) was detected.



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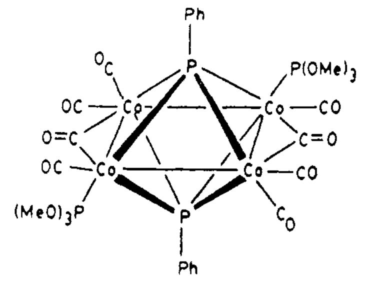

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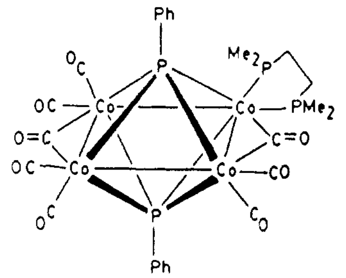

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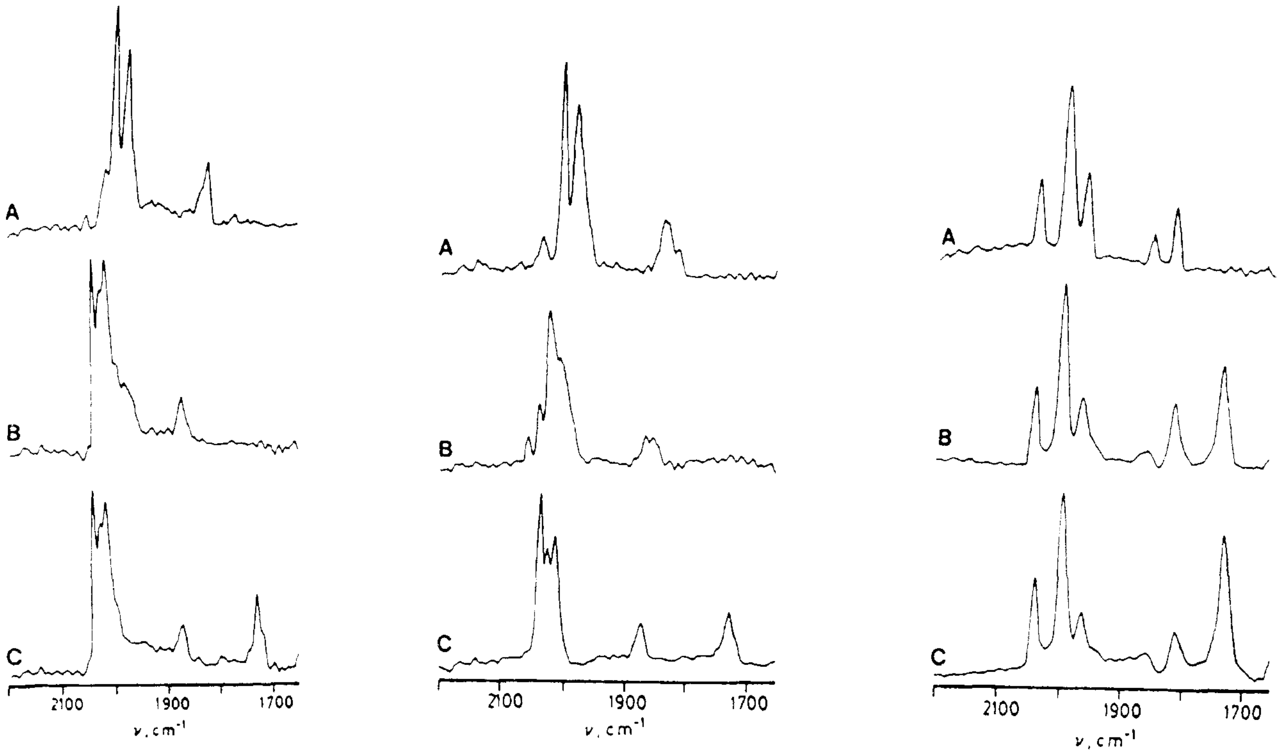


Figure 19. (a, left) CIR-FTIR of **1** in benzene with H_2/CO (600 psi): (A) 340 °C, (B) 130 °C, 48 h, (C) 150 °C, 24 h. (b, middle) CIR-FTIR of **2** in benzene with H_2/CO (600 psi): (A) 34 °C, (B) 130 °C, 48 h, (C) 150 °C, 36 h. (c, right) CIR-FTIR of **3** in benzene with H_2/CO (600 psi): (A) 34 °C, (B) 130 °C, 30 h, (C) 150 °C, 48 h. (Reprinted from ref 271; copyright 1992 Elsevier Sequoia S. A.)

$$RCH{=}CH_2 + CO/H_2 \xrightarrow{\text{catalyst}} RCH_2CH_2CHO + RCH(CH_3)CHO \quad (7)$$

use for this reaction inspired a large body of research in the 1970s which demonstrated the intermediacy of cluster carbonyl compounds. Work on cluster-catalyzed hydroformylation continued into the 1980s and early 1990s.

Metal clusters have been proposed to be the active catalyst in many hydroformylation studies. One approach to demonstrating cluster catalysis is by simple recovery of clusters quantitatively after a catalytic run. Fragmentation of clusters to mononuclear species is prevented by employing bridging ligands such as μ_4-PPh in $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$. Direct evidence supports the claim that this cluster stayed intact during hydroformylation on the basis of in situ infrared analysis: CIR spectroscopy.[271] In Figure 19, the CIR results are shown for hydroformylation of 1-pentene (eq 8) using three different clusters. Cluster 1, shown at the top of Figure 19a, is converted to $Co_4(CO)_9(PPh_3)(\mu_4\text{-}PPh)_2$ upon pressurization. Cluster 2 forms $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$ upon pressurization and heating to 130 °C. Finally, cluster 3 remained unchanged during the catalytic run due presumably to the presence of the chelating DMPE ligand.[271] These and related cobalt clusters were described as hydroformylation catalysts some 10–15 years earlier.[272,273]

$$\text{1-pentene} \xrightarrow[\substack{600\text{ psi } H_2/CO\\ 130\ ^\circ C}]{\substack{\text{cluster (0.25 mmol)}\\ \text{benzene}}} \text{hexanal} + \text{2-methylpentanal} \quad (8)$$

An excellent summary of recent data answers questions regarding true cluster catalysis in hydroformylation catalyzed by $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$.[274] Kinetic measurements at 150 °C showed that the TF decreased sharply with increased cluster concentration. This data supported fragmentation of the cluster, presumably to lower nuclearity molecules, e.g. $HCo(CO)_4$. However, data taken at 140 °C showed no decrease in TF with increased cluster concentration, supporting catalysis by an intact Co_4 cluster at this temperature.

Table 20. Product Selectivities in 1-Octene Hydroformylations Catalyzed by $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$[a] and $Co_2(CO)_8$ with and without Added PPh_3[b] (Reprinted from Ref 274; Copyright 1992 Marcel Dekker, Inc.)

				aldehyde n/b selectivity[c]			alcohol/aldehyde at		
entry	catalyst	amount catalyst (mmol)	temperature (°C)	5 h	10 h	20 h	5 h	10 h	20 h
1	$Co_2(CO)_8$	0.1	140		0.82	0.84	0.024	0.040	0.105
2	$Co_4(CO)_{10}(PPh_3)_2$	0.1	140		1.2	1.3	0	0	0.030
3	$Co_2(CO)_8/PPh_3$	0.1/0.1	140		1	1	0.05	0.09	0.16
4	$Co_4(CO)_{10}(PPh)_2/PPh_3$	0.1/0.1	140		1.1	1.1	0	0	0
5	$Co_4(CO)_{10}(PPh_3)_2/Co_2(CO)_8$	0.04/0.01	140		1.1	2	0.01	0.020	0.043
6	$Co_4(CO)_{10}(PPh_3)_2/Co_2(CO)_8$	0.05/0.05	140	1	1	1.5	0.06	0.06	0.10
7	$Co_2(CO)_8$	0.1	150			0.9		0.16	0.20
8	$Co_4(CO)_{10}(PPh_3)_2$	0.1	150	1.1	1.0	1.0	0.01	0.017	0.10
9	$Co_2(CO)_8/PPh_3$	0.1/0.1	150	1.0	1.0	0.9		0.47	0.70
10	$Co_4(CO)_{10}(PPh_3)_2/PPh_3$	0.1/0.1	150	1.1		1.0	0	0.01	0.04
11	$Co_4(CO)_{10}(PPh_3)_2/PPh_3$	0.1/0.4	150	1.1		1.0	0	0	0.01

[a] $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$ is cluster 1. [b] All reactions were carried out in mixed xylene solvent (20 mL) and toluene (10 mL) using 1-octene (30 mL, 190.5 mmol) and CO/H_2 (1:1, 800 psig). [c] n/b = ratio of normal to branched aldehydes.

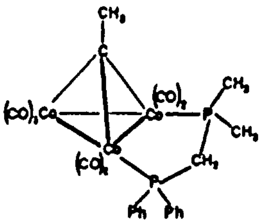


Figure 20. The structure of $(\mu_3\text{-}CH_3C)Co_3(CO)_7^-$ (dppm). (Reprinted from ref 277; copyright 1986 the American Chemistry Society.)

Indirect evidence of hydroformylation catalyzed by intact clusters was shown by variations in product selectivity. Table 20 gives the results of several different cobalt species. It is assumed that $Co_2(CO)_8$ forms $HCo(CO)_4$ under reaction conditions. The $Co_2(CO)_8$ catalyst produces more alcohol byproduct than catalysis by the Co_4 cluster at 140 °C. Other product differences and the effect of added phosphine on the product distribution further supported catalysis via an intact cluster at 140 °C. This result was also supported by in situ IR analysis similar to that shown in Figure 19.

Hydroformylation has been catalyzed by cobalt clusters based on the cobalt trimer and μ_3-CR bridge. As in the cases above, cluster breakdown during catalysis can be prevented by using a chelating diphosphine ligand. The cluster $(\mu_3\text{-}CCH_3)Co_3(CO)_9$ was completely degraded in the presence of 1-pentene under 80 bar pressure of H_2/CO (1:1) at 130 °C. Only traces of aldehyde were observed after 24 h. In another study, $RCo_3(CO)_9$ clusters were prepared where R was polymerizable. The derived polymers, $\text{-(}R\text{-}Co_3(CO)_9\text{)-}_n$, catalyzed hydroformylation where the actual catalyst[275] appears to contain one or two metal atoms. An analogous cluster was examined as a catalyst which contained a chelating diphosphine ligand, dppm. When 1-pentene and $(\mu_3\text{-}CCH_3)Co_3(CO)_7$(dppm) were combined under 80 bar of H_2/CO at 130 °C for 24 h, a 22% yield of 2-methylpentanal and hexanal was obtained.[276]

The structure of $(\mu_3\text{-}CCH_3)Co_3(CO)_7$(dppm) suggested the possibility of synthesizing a chiral cluster and using it to catalyze synthesis of chiral products via hydroformylation. The cluster in Figure 20 was indeed chiral, although it was obtained as a racemic mixture. The cluster in Figure 20 was employed as a catalyst for hydroformylation of styrene, 80 bar of H_2/CO, 105 °C. A 23% yield of mostly branched aldehyde was obtained. Unfortunately, no optical induction in the products was achieved.[277] A series of clusters of the type $(\mu_3\text{-}PhC)Co_3(CO)_8L$ ($L = PPh_3, AsPh_3,$ and $SbPh_3$) were prepared and tested for catalytic activity in the hydroformylation of styrene and diisobutene. The arsine-substituted cluster gave all normal aldehyde products.[278]

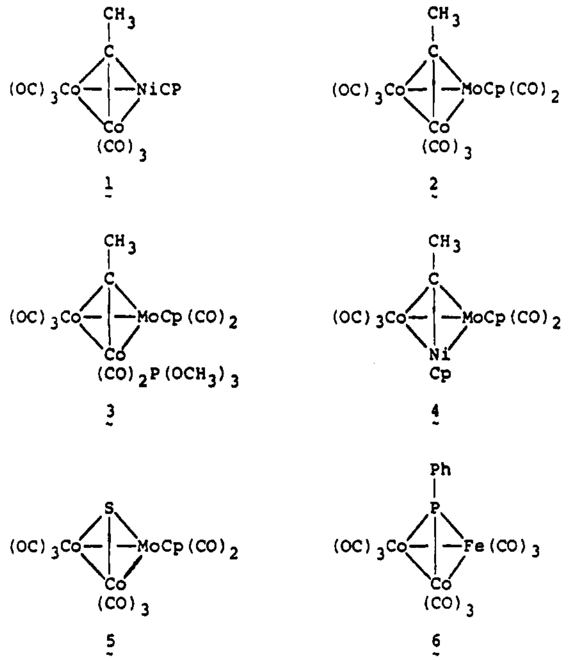


Figure 21. Some mixed Co–M clusters active as hydroformylation catalysts. (Reprinted from ref 279; copyright 1984 Elsevier Sequoia S. A.)

Two patented reports describe reactions that employ cobalt catalysts which may be colloidal in nature. In one case, various cobalt carbonyl precursors were decomposed in the presence of various copolymers, such as styrene–4-vinylpyridine copolymer or styrene–*p*-styryldiphenylphosphine oxide copolymer.[69] In another case, a Co colloid was stabilized by various polymers such as hydroxy-terminated styrene–butadiene copolymer or styrene–*p*-styryldiphenylphosphine copolymer.[66] The cobalt materials were employed as hydroformylation catalysts of 1-hexene.

A variety of Co_xM_y mixed-metal clusters has been employed as hydroformylation catalysts.[279] One set of clusters, shown in Figure 21, were active catalysts for hydroformylation of 1-pentene and styrene. The Co–Fe cluster (6, Figure 21) was shown to form the mononuclear catalyst $HCo(CO)_4$ under reaction con-

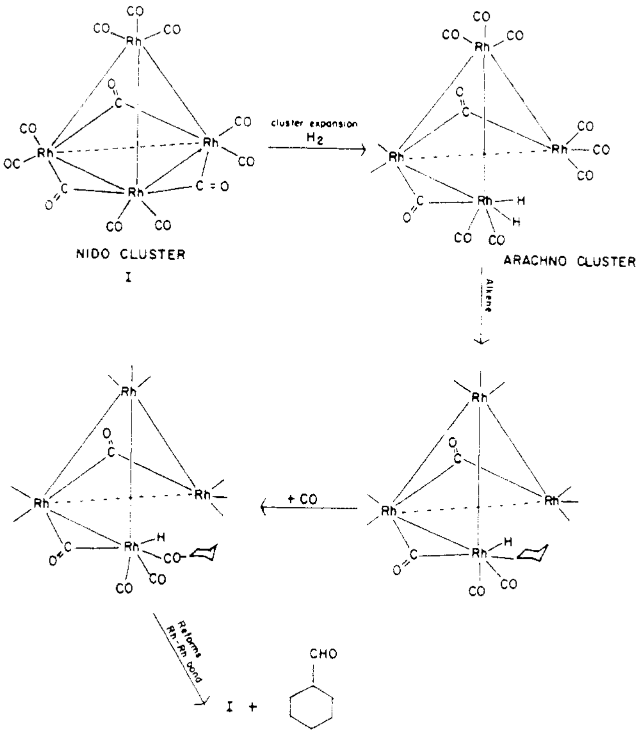


Figure 22. Proposed mechanism of hydroformylation catalyzed by $Rh_4(CO)_{12}$. (Reprinted from ref 295; copyright 1988 Elsevier Sequoia S. A.)

ditions. However, the other clusters could be recovered unchanged after a catalyst run. Furthermore, the clusters 1-5 in Figure 21 did not produce observable amounts of other fragmented products at 130 °C and 600 psi H_2/CO. The hydroformylation reactions were carried out at 60 °C, making cluster fragmentation under catalytic conditions highly unlikely.

The mixed Co-Fe cluster $Fe_2Co_2(CO)_{11}(\mu_4\text{-}PPh)_2$ was a catalyst for hydroformylation of 1-pentene.[280] Unlike the cluster **6** in Figure 21, the Fe_2Co_2 cluster stays intact during catalysis. Catalysis via an intact cluster was demonstrated with in situ CIR IR spectroscopic analyses. Additional work on mixed Fe_xCo_y clusters as hydroformylation catalysts has been published,[281-285] as has work on mixed metal Co-Ru[283] and Co-Pt[223] clusters.

A variety of $Rh_4(CO)_{12-x}L_x$ clusters (L = phosphine or phosphite, x = 1-4) and $Co_{4-n}Rh_n(CO)_{12}/xL$ (n = 0, 2; x = 0-9) clusters were examined as hydroformylation catalysts for 1-pentene, styrene, and cyclohexene.[286] The all rhodium clusters appeared to remain intact during catalysis. While $Co_4(CO)_{12}$ and $Co_4(CO)_{12-x}(P(OPh)_3)_x$ (x = 1-3) clusters were inactive, the mixed Co_xRh_y cluster was more active than $Rh_4(CO)_{12}$. Synergistic improvement in catalytic activity has been described in other systems.[223,283,285,287]

Hydroformylation using all substituted rhodium carbonyl clusters has been reported by several groups.[288-291] A common theme to this work was the need for added ligand to achieve high catalytic rates. These added ligands include phosphines, arsines, stilbines, and phosphites. Catalysis via clusters is implied because the required additional ligand helps to maintain cluster integrity.

A history of the work using unsubstituted rhodium carbonyl clusters in hydroformylation is briefly summarized.[292] Most work has shown mononuclear species present in situ and/or after catalysis. One of the proposed intermediates is $(RCO)Rh(CO)_4$ which has been observed in in situ high-pressure IR studies. A detailed kinetic analysis confirms the formation of acyl-substituted mononuclear rhodium carbonyl under hydroformylation conditions from $Rh_4(CO)_{12}$. Other work on this cluster has appeared.[158,293] Rhodium cluster formation was the *cause* of catalyst deactivation in one study. Declusterification to form low molecular weight

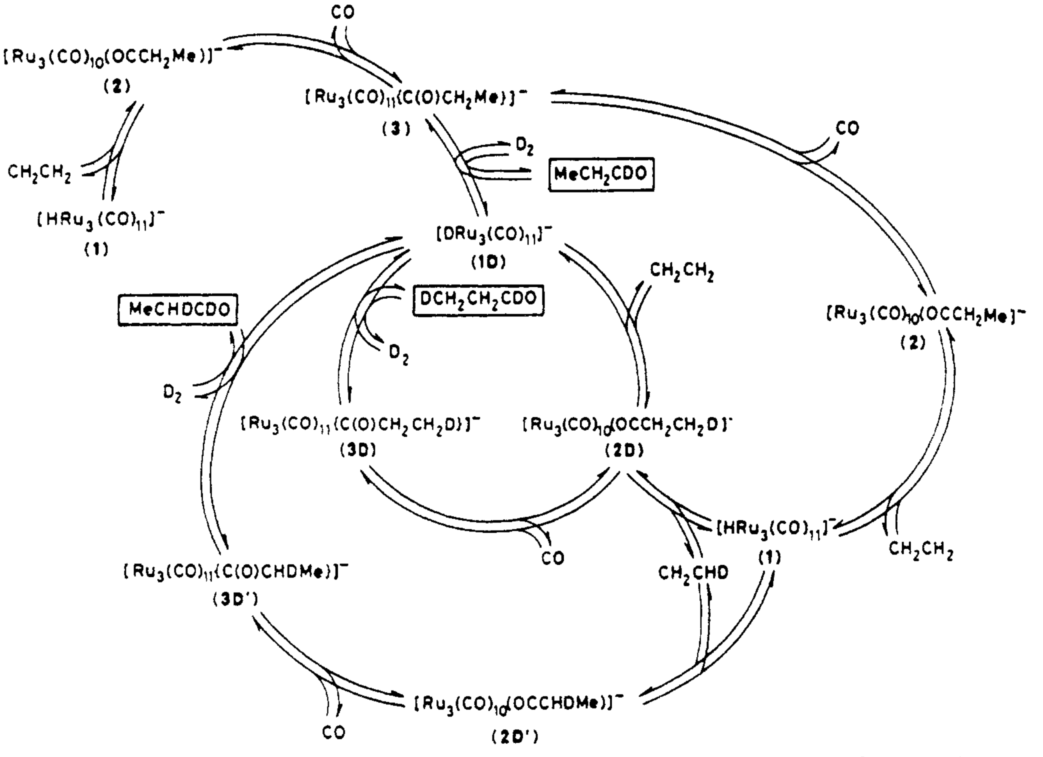


Figure 23. Deuterioformylation of ethylene with $[HRu_3(CO)_{11}]^-$, 1, as the catalyst. (Reprinted from ref 297; copyright 1985 the Royal Society of Chemistry.)

Table 21. Hydroformylations of 1-Pentene with 1:1, H_2/CO at 800 psi Catalyzed by Several Cluster Systems Containing More Than One Transition Metal Element in Benzene[a] (Reprinted from Ref 301; Copyright 1985 Elsevier Sequoia S. A.)

catalyst					products[b]	
no.	formula	temp (°C)	time (h)	conversion[b] (%)	hexanal	2-methylpentanal
1	$Pd_2Mo_2(\eta\text{-}Cp)_2(\mu_3\text{-}CO)_2(\mu_2\text{-}CO)_4(PPh_3)_2$	95	17	0		
5	$Pt_2Mo_2(\eta\text{-}Cp)_2(\mu_3\text{-}CO)_2(\mu_2\text{-}CO)_4(PPh_3)_2$	95	17	0		
10	(diphos)$PtCo_2(\mu_2\text{-}CO)(CO)_6$	60	15	0		
10	(diphos)$PtCo_2(\mu_2\text{-}CO)(CO)_6$	80	21	39	30.7	8.2
11	(diars)$PtCo_2(\mu_2\text{-}CO)(CO)_6$	80	22	0		
12	$(CO)_4CoPt(C_6H_{11}NC)_2Co(CO)_4$	62	20	0		
12	$(CO)_4CoPt(C_6H_{11}NC)_2Co(CO)_4$	100	20	39.3	30	9.3
14	$Pt_2Co_2(\mu\text{-}CO)_3(CO)_5(PPh_3)_2$	62	17	trace	trace	trace
14	$Pt_2Co_2(\mu\text{-}CO)_3(CO)_5(PPh_3)_2$	75	18	16.5	14	2.5
14	$Pt_2Co_2(\mu\text{-}CO)_3(CO)_5(PPh_3)_2$	100	17	85.4[c]	63.5	14.6

[a] Each reaction was run using 9 mmol of 1-pentene, 0.01 mmol of catalyst, and 4 mL of benzene with the exception of the reactions using catalyst 14, where 4 mL of toluene was used. [b] Mole percentages were based on 1-pentene charged. [c] 7.3% of 1-hexanol was also present.

Table 22. Group 8 and 9 Transition Metal Chlorides as Catalyst Precursors in Homogeneous Hydroformylation of 1-Hexene[a] (Reprinted from Ref 302; Copyright 1992 Elsevier Sequoia S. A.)

metal chloride	amine	solvent	C_7 aldehydes (%)	n:i ratio	C_7 alcohols (%)	n:i ratio
$FeCl_3$	-	ethanol	0		0	
$FeCl_3$	NEt_3	ethanol	0		0	
$RuCl_3{\cdot}3H_2O$[b]	-	acetone	6		0	
$RuCl_3{\cdot}3H_2O$[b]	NEt_3	acetone	16		0	
$RuCl_3{\cdot}3H_2O$[b]	-	toluene	0		0	
$RuCl_3{\cdot}3H_2O$[b]	NEt_3	toluene	9		0	
$Co/Cl_2{\cdot}6H_2O$	-	acet/tolu	97	0.7	0	
$CoCl_2{\cdot}6H_2O$	NEt_3	acet/tolu	75	2.4	0	
$CoCL_2{\cdot}6H_2O$	-	toluene	2		3	
$CoCl_2{\cdot}6H_2O$	NEt_3	toluene	6		0	
$RhCl_3{\cdot}3H_2O$	-	ethanol	41	0.2	0	
$RhCl_3{\cdot}3H_2O$	NEt_3	ethanol	4		68	1.1
$RhCl_3{\cdot}3H_2O$	-	toluene	2		0	
$RhCl_3{\cdot}3H_2O$	NEt_3	toluene	1		98	0.7
$IrCl_3$	-	ethanol	2		0	
$IrCl_3$	NEt_3	ethanol	2		0	
$IrCl_3$	-	toluene	18	0.2	1	
$IrCl_3$	NEt_3	toluene	12	1.0	2	

[a] Conditions: $P(CO/H_2)$ = bar; T = 100 °C; react. time = 17 h; n(metal species) = 0.1 mmol; V(solvent) = 3.0 cm^3; $n(NEt_3)$ = 0.79 mmol; V(1-hexene) = 1.0 cm^3; V(benzene as internal standard) = 0.2 cm^3. [b] n(metal species) = 0.07 mmol.

Table 23. Group 8 and 9 Transition Metal Carbonyls as Catalyst Precursors in Homogeneous Hydroformylation of 1-Hexene[a] (Reprinted from Ref 302; Copyright 1992 Elsevier Sequoia S. A.)

metal carbonyl	amine	solvent	C_7 aldehydes (%)	n:i ratio	C_7 alcohols (%)	n:i ratio
$Fe_3(CO)_{12}$	-	toluene	7		0	
$Fe_3(CO)_{12}$	NEt_3	toluene	7		0	
$Ru_3(CO)_{12}$[b]	-	toluene	96	1.0	2	
$Ru_3(CO)_{12}$[b]	NEt_3	toluene	50	1.1	26	3.3
$Os_3(CO)_{12}$	-	CH_2Cl_2	14	2.2	0	
$Os_3(CO)_{12}$	NEt_3	CH_2Cl_2	0		0	
$Co_2(CO)_8$	-	toluene	84	2.0	1	
$Co_2(CO)_8$	NEt_3	toluene	85	1.7	0	
$Co_4(CO)_{12}$	-	toluene	74	2.8	1	
$Co_4(CO)_{12}$	NEt_3	toluene	82	2.2	0	
$RhH(CO)(PPh_3)_3$[c]	-	toluene	98	1.2	0	
$RhH(CO)(PPh_3)_3$[c]	NEt_3	toluene	93	1.9	4	
$Rh_2(CO)_4Cl_2$	-	toluene	99	0.8	0	
$Rh_2(CO)_4Cl_2$	NEt_3	toluene	0		97	0.7
$Rh_4(CO)_{12}$	-	toluene	95	0.6	0	
$Rh_4(CO)_{12}$	NEt_3	toluene	0		100	1.0
$Rh_4(CO)_8(P(OPh)_3)_4$	-	toluene	96	1.6	1	
$Rh_4(CO)_8(P(OPh)_3)_4$	NEt_3	toluene	94	1.2	1	

[a] Conditions: $P(CO/H_2)$ = 50 bar; 100 °C; react. time = 17 h; n(metal species) = 0.1 mmol; V(solvent) = 3.0–5.0 cm^3; $n(NEt_3)$ = 0.79 mmol; V(1-hexene) = 1.0 cm^3; V(benzene as internal standard) = 0.2 cm^3. [b] n(metal species) = 0.08 mmol. [c] Conditions: $P(CO/H_2)$ = 54 bar; T = 60 °C; react. time = 4.5 h.

clusters occurred under reaction conditions to regenerate active catalysts.[294]). The

Catalysis with $Rh_4(CO)_{12}$ was examined under mild conditions in an effort to confirm intact clusters under reaction conditions.[295] A proposed mechanism is shown in Figure 22. Previous kinetic work under more forcing conditions indicated cluster dissociation. The evidence for catalysis by the intact cluster shown in Figure 22 is supported by observing first-order dependence on the Rh_4 cluster. Additional kinetic and spectroscopic data support the catalytic cycle in Figure 22. The $Rh_4(CO)_{12}$ cluster was also active for hydroformylation of enynes.[296]

The ruthenium cluster $HRu_3(CO)_{11}^{-2}$ was examined as a catalyst for the hydroformylation of 1-propene.[297,298] The product chemoselectivity was independent of variations in solvent, temperature, and total pressure. Regioselectivity varied according to solvent. For example, in acetonitrile a ratio of 92.3% *n*-butanal and 7.7% isobutanal was obtained while in glyme a product ratio of 98.0% *n*-butanal and 2.0% isobutanal was obtained. The high selectivity supported catalysis via an intact Ru_3 unit.[298]

Earlier work on hydroformylation of ethylene by $HRu_3(CO)_{11}^-$ concluded that catalysis was due to an intact Ru_3 center on the basis of an isotope labeling study.[297] A mechanism is shown in Figure 23 which is supported by the results of the labeling study. Still earlier work using this Ru_3 cluster suggested intact catalysis for hydroformylation, hydrogenation, sila carbonylation, and hydrosilylation.[220] One study reports the use of $Ru_3(CO)_9(Ph_2P\text{-}m\text{-}C_6H_4SO_3Na)_3$ for hydroformylation of propylene in an aqueous solution where the catalyst is water soluble.[298] In a typical run where propylene is reacted with CO/H_2 in water in the presence of the water-soluble Ru_3 cluster, a 15.9 normal/isobutyraldehyde (n/i) mixture is obtained. This compares to the 20 n/i ratio obtained when propylene was reacted with CO/H_2 in DMF in the presence of $[Ru_3(CO)_{11}]^-$.[220]

Only a few reports have appeared since 1980 for hydroformylation catalyzed by other metals. The use of unsupported iron colloids has been described in one case[67] while polymer-supported colloids have been reported for Ru, Rh, Os, and Ir.[299,300] In this case, metal carbonyl precursors were decomposed onto the polymer supports. Two studies examined a large number of compounds for hydroformylation catalytic activity[301,302] (Tables 21–23). The reverse of hydroformylation, dehydration of alcohols, was catalyzed by a mixed Pd–Mo cluster $Na_2[Pd_4(CpMo(CO)_3)_4]$.[303]

H-H and C-H Activation

Activation of H–H and C–H bonds by transition metals is a critical step in many catalytic reactions. Most investigations have examined supported catalysts.[137–139] Several reports show that unsupported metal clusters in the gas-phase-catalyzed H–H and C–H activation. Clusters are generated by laser vaporization and gas aggregation techniques. The activity of iron clusters is dependent on size. Constant and high activity is found for Fe_n, $25 < n < 270$. For clusters of $n \geq 8$, activity varies with n. The size-selective behavior may reflect the competition between Pauli repulsion, which creates a barrier to H–H chemisorption, and attractive partial charge transfer interactions.[304,305] Hydrogen activation on Pd, Ni, Pt, and Rh clusters in the gas phase has been investigated as well.[305]

C–H bond activation has also been studied by clusters generated in the gas phase. Methane was unreactive toward clusters of iron, rhodium, and aluminum. However, palladium and platinum clusters react with methane, each with its own size selectivity, Figure 24. For Pt_n clusters, the $n = 2$–5 size range is most reactive, whereas for Pd_n the $n = 7$–16 clusters are most reactive.[304] Further details of these size–activity effects have been reported.[305]

There is at least one example of a metal-cluster-catalyzed C–H activation. The rhodium clusters $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ under CO pressure catalyze addition of a C–H bond of benzene to unsaturated substrates. The unsaturated substrates include diphenylketene, isocyanates, acetylenes, and olefins.[258] Equilibration of H_2 and D_2 is catalyzed by several mixed platinum–gold clusters. These clusters include $[Pt(AuPPh_3)_8](NO_3)_2$ and $[(PPh_3)_2]Pt(AuPPh_3)_3](NO_3)$. A mechanism for the reaction does *not* include a step whereby the cluster degrades to a monomeric platinum phosphine species because such a species was tested and had much poorer activity than the mixed metal cluster. Formation of HD from H_2 and D_2 probably involves formation of an intermediate whose metal core resembles $PtAu_x(H_2)(D_2)$.[306]

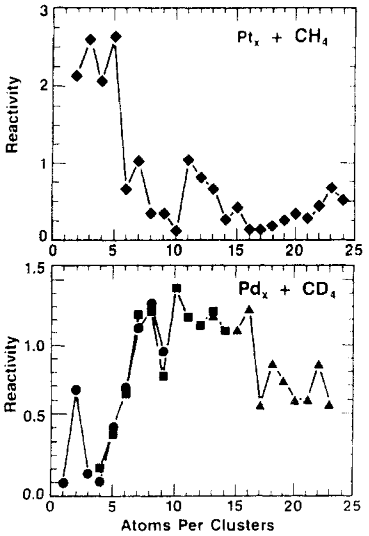


Figure 24. Relative activity of platinum (top) and palladium (bottom) clusters toward methane. (Reprinted from ref 304; copyright 1990 the American Chemical Society.)

Hydrosilylation

In the 1940s and 1950s, hydrosilylation (eq 9) was catalyzed by supported platinum group metal catalysts.

$$R_3SiH + R'CH{=}CH_2 \xrightarrow{\text{catalyst}} R_3SiCH_2CH_2R' \quad (9)$$

In the late 1950s, the first soluble catalyst, H_2PtCl_6, in 2-propanol (Speier's catalyst) was introduced.[307] The widely accepted Chalk–Harrod mechanism for platinum-catalyzed hydrosilylation was based on the intermediacy of molecular platinum complexes.[308] Like the well-known hydrogenation reaction, where a key step is oxidative addition of H–H to a metal center, the Chalk–Harrod mechanism proposed Si–H oxidative addition to a metal center.[22]

The "colloid surprise section" below describes the reduction of platinum group metal colloids by SiH compounds. Compounds containing the SiH functionality, especially those with electronegative substituents, are effective reducing agents for platinum group metal compounds.[51] The products from these reductions are colloidal solutions. Hydrosilylation reactions often have an induction period or a slow reaction regime.[309] The onset to high-percent conversion corresponds to the reaction's exotherm, formation of the characteristic yellow color, and colloid formation.[119] Additional support has been published for catalysis by platinum[56–58,309–311] and rhodium[51,59,312,313] colloids.

Analyses by TEM of a typical hydrosilylation reaction, such as the platinum-catalyzed reaction between hexene and Et_3SiH, revealed colloids. These reactions were inhibited by mercury but not by dct. Both complementary tests support colloidal and argue against catalysis by mononuclear compounds. Reactions run with neohexene turned yellow and went to high conversion while the reaction run with n-hexene remained colorless with poor conversion to product. Figures 25 and 26 contrast the morphology of the platinum colloids formed in these two reactions. The yellow solutions from the neohexene and Et_3SiH reaction gave 22–28 Å diameter crystallites. The diameter of these particles corresponded to the $n = 5$ shell clusters (Table 2, Figure 25) or 561 atoms. The colorless solutions from the platinum colloid (Figure 26) from the n-hexene and Et_3SiH reaction contained 15–20 Å diameter particles consistent with $n = 4$ shell clusters or 309 atoms.[309]

Some reports in the patent literature describe acceleration of the hydrosilylation reaction either by

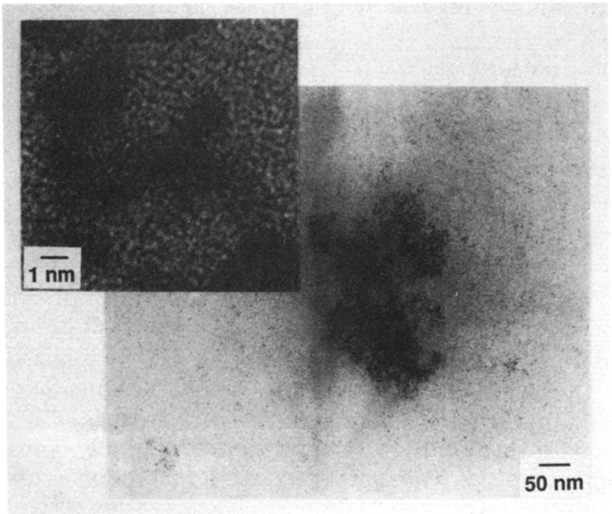


Figure 25. TEM (HREM in inset) of Pt colloid formed in the platinum-catalyzed reaction between Et_3SiH + $H_2C{=}CHC(CH_3)_3$. (Reprinted from ref 309a; copyright 1991 Academic Press.)

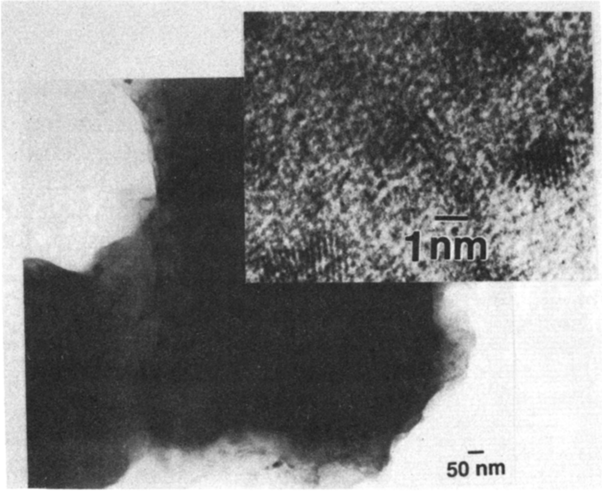


Figure 26. TEM (HREM in inset) of Pt colloid formed in the platinum-catalyzed reaction between $Et_3SiH + H_2C{=}CH_2$-$CH_2CH_2CH_2CH_3$. (Reprinted from ref 309b; copyright 1991 Academic Press.)

prereaction of the platinum catalyst with an SiH compound[314] or by addition of a "second hydrosilane" to promote the reaction.[315] The results suggest colloid formation as an explanation for the observed acceleration by added SiH. The nickel catalyst used in hydrogenation of alkenyl chlorosilanes is accelerated by prereaction with SiH.[316] This acceleration may represent a general trend of prereduction to reduced or colloidal metal catalysts.

Clusters have been reported as hydrosilylation catalysts. The cluster $[HRu_3(CO)_{11}]^-$ is a catalyst for both silacarbonylation and hydrosilylation of ethylene and propylene. In the presence of CO, the ruthenium cluster catalyzes conversion of ethylene and Et_3SiH to a mixture of (triethylsiloxy)propenes. In the absence of carbon monoxide, a mixture of unsaturated and saturated silanes forms. Metal carbonyl compounds, of unknown identity, form during catalysis.[220] Photoinitiated hydrosilylation of triethylsilane and acetophenone was catalyzed by the following clusters: $[((CO)_3Co)_2(CpMo(CO)_2)(\mu_3\text{-}CCH_3)]$, $[((CO)_3Co_2(CpNi)(\mu_3\text{-}CCH_3]$, $[(Co(CO)_3)(CpMo(CO)_2)(CpNi)(\mu\text{-}CCH_3)]$, and other mixed Co, Fe, W, and Ni clusters. The criterion described above for catalysis via mixed-metal systems suggests catalysis by intact clusters.[160] Other photoinitiated hydrosilylations catalyzed by mixed-metal clusters have been reported.[301]

Hydrosilylation appears to occur via mononuclear (not cluster or colloid) intermediates when ligands prevent colloid formation. Hydrosilylation of vinyl and vinylidene-type olefins was mediated by $PtCl_2$/substrate mixtures containing triphenylphosphine. The phosphine prevents colloid formation.[317] Hydrosilylation of styrene is catalyzed by $Cl_2Pt(PhCH{=}CH_2)_2$. Mechanism studies strongly support the intermediacy of mononuclear platinum compounds.[318]

Attempts to carry out hydrosilylation of epoxy-containing olefins often lead to polymerization of the epoxy functionality. Platinum and rhodium catalysts, without phosphine, form colloids under hydrosilylation conditions. The colloids catalyze the ring opening polymerization of epoxides. Mercury inhibits the epoxy polymerization. However, phosphine ligands prevent colloid formation. Platinum and rhodium catalysts with phosphines catalyze hydrosilylation of olefins (at a lower rate than catalysts without phosphine) but are inactive for epoxy polymerization.[319,320]

Isomerization

Olefin isomerization is unequivocally catalyzed by clusters and colloids.[10b,11] As described above, one criterion for demonstrating cluster catalysis is if enhanced reactivity is observed when a catalyst is composed of two or more different metal atoms and the activity differs from the individual components. The cluster $H_4Ru_4(CO)_{12}$ catalyzed the hydrogenation and isomerization of pent-1-ene. However, enhanced reactivity occurs when gold is incorporated into the cluster framework (Table 24). Surprisingly, mononuclear gold is inactive. While the origin of the enhancement by gold (but not by copper) is not known, these results strongly support catalysis by intact clusters.[226] Other mixed-metal ruthenium–gold clusters catalyze olefin isomerization as well.[321]

A mixed-metal Ni–Ru cluster, $CpNiRu_3(\mu\text{-}H)_3(CO)_9$, selectively catalyzes hydrogenation and isomerization of double bonds. The presence of both metals is important in the catalysis, indicating cluster catalysis.[234] Olefin isomerization is catalyzed by at least one other mixed-metal system, $Co_2Pt_2(CO)_8(PPh_3)_2$.[223] Ruthenium carbonyl clusters with and without bridging phosphido groups catalyze isomerization of *cis*- to *trans*-stilbene. The cluster $HRu_3(CO)_9(PPh_2)$ is more active as an olefin hydrogenation catalyst than $Ru_3(CO)_9(PPh_2H)$, while the order in activity is reversed for isomerization. Cluster catalysis was proposed for the ruthenium systems.[232] A related set of iron clusters, such as $Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}PR)$ (R = iPr, $PNEt_3$), also catalyze the stilbene isomerization, a mechanism may involve nido–closo transformation of the cluster.[231]

Several clusters participate in equilibria between clusters and mononuclear species. Mononuclear Pd(0) compounds form via fragmentation of $[Pd_4phen_4(CO)_4][OAc]_4$. These mononuclear species are likely responsible for olefin isomerization catalyzed by the Pd_4 cluster.[209] In contrast, the Co_3 cluster $HCo_3(CO)_9$

Table 24. Isomerization and Hydrogenation of Pent-1-ene[a] (Reprinted from ref 226; copyright 1985 the Royal Society of Chemistry.)

catalyst source	conversion (%)	product proportions (%) of total C_5 organics		
		pentane	*trans*-pent-2-ene	*cis*-pent-2-ene
$[Au(PPh_3)Cl]$	0			
$[H_4Ru_4(CO)_{12}]$ (**5**)	32.9	1.7	19.8	11.0
$[(Ph_3P)_2N[[H_3Ru_4(CO)_{12}]$ (**6**)	7.9		4.5	3.4
$[H_3Ru_4\{Au(PPh_3)\{(CO)_{12}]$ (**1**)	71.0	1.4	51.4	18.2
$[H_2Ru_4\{Au(PPh_3)\}_2(CO)_{12}]$ (**3**)	49.6	1.1	33.1	15.3
$[H_3Ru_4\{Cu(PPh_3)\}(CO)_{12}]$ (**2**)	29.4	0.3	18.5	10.7
$[H_2Ru_4\{Cu(PPh_3)\}_2(CO)_2]$ (**4**)	7.7		4.4	3.3

[a] Reaction conditions: 2.0 mM catalyst source; 54 mM pent-1-ene; solvent, CH_2Cl_2, 2.5 mL; 1 atm H_2, 35.0 ± 0.2 °C, 24 h.

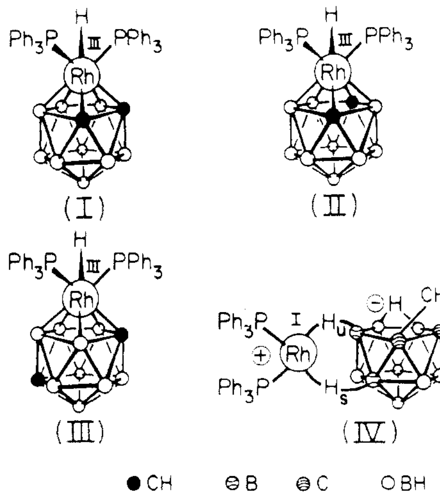


Figure 27. Structures of rhodacarboranes (**I–IV**) which were employed in catalytic alkene isomerization reactions. (Reprinted from ref 229; copyright 1984 the American Chemical Society.)

takes part in the equilibrium reaction of eq 10. Neither

$$HCo(CO)_4 + Co_2(CO)_8 \rightleftharpoons HCo_3(CO)_9 + 3CO \qquad (10)$$

$HCo(CO)_4$ nor the dimer were catalytically active for isomerization of 1-hexene at 0 °C. The trimer was active. These and other results suggest catalysis via the trimer.[71]

There are extensive studies on the synthesis and structure of metallocarboranes.[228] Several Rh carboranes (Figure 27) catalyze 1-hexene isomerization. Not surprisingly, the metallocarborane remains intact during catalysis. The proposed mechanism requires the closo clusters (**I–III** in Figure 27) to tautomerize to a species with a highly active Rh(I) center.[229]

Metal colloids are catalysts for olefin isomerization. Disproportionation of deuterio-substituted 1,4-cyclohexadiene is catalyzed by colloidal nickel. Key steps in the proposed mechanism are fundamentally related to isomerization reactions.[181] A very active area of research in the 1980s was the synthesis of "unsupported" metal colloids in a variety of solvents using metal atom reactor techniques. One study described the synthesis of Ni, Co, and Fe in pentane, toluene, and C_4F_8 and their catalytic activities for hydrogenation and isomerization of butenes and butadiene. The catalytic activity of the unsupported catalysts was compared to those on various supports (termed SMAD for *s*olvated *m*etal *a*tom *d*ispersed catalysts) (Tables 25 and 26).[174] The supported catalysts were clearly more active than the unsupported colloids.

A series of mixed $Pt_{100-x}Au_x$ ($0 < x < 100$) colloids (Figure 14) were active catalysts for hydrogenation, dehydrogenation, and isomerization of *n*-butane. These runs involved catalysts *derived* from colloids and deposited on a graphite support. Isomerization activity peaked for the mixed-metal colloid composition $x = 20$.[108] As described earlier, the fact that an optimum composition for catalysis exists supports cluster catalysis.

Oligomerization

Mixed-metal Co–Pt carbonyl clusters have been employed as catalysts for the cyclooligomerization of 1,3-butadiene.[223] The clusters $Pd_2Mo_2Cp_2(\mu_3\text{-}CO)_2(\mu_2\text{-}CO)_4(PPh_3)_2$ and $Pt_2W_2Cp_2(\mu_3\text{-}CO)_2(\mu_2\text{-}CO)_4(PPh_3)_2$ catalyzed formation of low molecular weight polymers of 1,3-butadiene. A mixture of 4-vinylcyclohexene, 1,5-cyclooctadiene, and cyclododecatriene also formed.[301] The cluster $Pt_5(CO)_6(PPh_3)_4$ catalyzed the oligomerization of 1,3-butadiene to give only polymeric product.[301]

Strong evidence for cluster catalysis is provided by a cobalt-cluster-catalyzed cyclotrimerization reaction. $Co_3(H)(CO)_3(PMe_3)_6$ catalyzes cyclotrimerization of phenylethyne. No known mononuclear compounds catalyze this reaction. Nevertheless, catalysis by a mononuclear species is still a possibility.[322]

However, this oligomerization is carried out on a SiO_2 support, so technically this result falls outside the range of this review. Nevertheless, the nickel trimer appears to stay intact during catalysis.[323] Finally, diene polymerization is catalyzed by π-stabilized clusters of alkali metals, such as Li–Na clusters.[324] Acetylene is polymerized by the Pd tetramer shown in eq 2.[208] Ethylene is oligomerized via $Cp_3Ni_3(CO)_2$.

Redox Reactions

Metal colloids are effective catalysts for redox reactions, Table 27,[325] where the key to effective catalysis is separation within a medium to prevent competitive radical recombinations or fast radiative or nonradiative relaxation processes.[325,326]

Some novel methods have been employed to stabilize the colloidal catalyst and thereby minimize back-electron transfer. Platinum colloids were prepared within a surfactant vesicle by irradiation of K_2PtCl_4. The surfactant vesicles were prepared by cosonicating dipalmitoylphosphatidylcholine with a surfactant. The catalytic efficiency of the vesicle-entrapped platinum colloids was demonstrated by the H_2-catalyzed reduc-

Table 25. Activities/Selectivities and Properties of Catalysts (Unsupported) (Reprinted from Ref 174; Copyright 1983 Elsevier Sequoia S. A.)

catalyst	rate of isomerization of 1-butene (% min^{-1} g^{-1})	rate of hydrogenation of butenes (% min^{-1} g^{-1})	rate of hydrogenation of 1,3-butadiene (% min^{-1} g^{-1})	selectivity to butenes from 1,3-butadiene	BET surface area by N_2 adsorption (m^2 g^{-1})	elemental composition (wt %/g of catalyst) C	H	F
Ni–toluene	26	24	20	good	30	2.72	0.24	
Co–toluene	0	25	6.2	good	10	3.14	<0.17	
Fe–toluene[a]	0	0	0	–	–	10.42	0.92	
Ni–pentane	26	3680	4110	poor	60	3.16	0.48	
Co–pentane	19	194	58	good	90	3.50	0.66	
Fe–pentane[a]	0	1.3	2.0	good	170	2.66	0.46	
Ni–C_4F_8	45	6420	11600	poor	90	1.67	0.59	1.66
Co–C_4F_8	0	21	19	good	100	3.08	0.32	2.95
Fe–C_4F_8	780	1680	2970	poor	130	1.83	0.42	1.53
Ni–Xe	0	0	0	–	20			
Co–Xe	0	0	0	–	40			
Fe–Xe	0	0	0	–	10			

[a] The reaction temperature was 25 °C for Fe–pentane and Fe–toluene. For the other catalysts, it was 0 °C.

Table 26. Activities/Selectivities and Properties of Catalysts (Supported) (Reprinted from Ref 174; Copyright 1983 Elsevier Sequoia S. A.)

catalyst	rate of isomerization of 1-butene [% min^{-1} (g of metal)$^{-1}$]	rate of hydrogenation of 1-butene [% min^{-1} (g of metal)$^{-1}$]	rate of hydrogenation of 1,3-butadiene [% min^{-1} (g of metal)$^{-1}$]	selectivity to butenes from 1,3-butadiene	total BET surface area by N_2 adsorption [m^2 (g of catalyst)$^{-1}$] catalyst	support only	metal surface area by H_2 adsorption [m^2 (g of metal)$^{-1}$]
22% Ni/Al_2O_3	245	22	17	good	140	170	30
5% Ni/Al_2O_3	64	14	26	intermediate	170	170	55
0.2% Ni/Al_2O_3	0	0	0	–	150	170	–
17% Co/Al_2O_3	759	4710	6240	poor	140	170	49
4% Co/Al_2O_3	4200	1780	85	good	150	170	52
0.9% Co/Al_2O_3	2890	389	0	–	160	170	–
70% Ni/SiO_2	267	4	5	good	230	270	31
8% Ni/SiO_2	93	11	10	good	260	270	37
2% Ni/SiO_2	0	0	0	–	280	270	–
9% Co/SiO_2	4780	6060	200	intermediate	230	270	59
4% Co/SiO_2	10000	2750	50	good	270	270	76
1% Co/SiO_2	6500	1800	20	good	270	270	–
15% Ni/SiO_2–Al_2O_3	2050	56	23	good		480	
4% Ni/SiO_2–Al_2O_3	3400	650	21	good		480	
7% Co/SiO_2–Al_2O_3	3340	4279	605	good		480	
4% Co/SiO_2–Al_2O_3	2040	551	38	good		480	
22% Ni/TiO_2	566	2420	3650	poor		68	
5% Ni/TiO_2	193	190	6	good		68	
11% Co/TiO_2	110	4390	8300	poor		68	
3% Co/TiO_2	0	0	0	–		68	
22% Ni/HY	571	9	13	good		860	
6% Ni/HY	1750	10	27	good		860	
18% Co/HY	870	932	3220	poor		860	
3% Co/HY	3690	117	121	good		860	

tion of either methylene blue or 10-methyl-5-deazaisoalloxazine-3-propanesulfonic acid. Reduced mixtures could be reoxidized with $FeCl_3$.[327]

Citrate-stabilized gold colloids are one of the oldest known colloid preparations. The reaction in eq 11 was

$$Fe(CN)_6^{3-} + S_2O_3^{2-} \rightarrow Fe(CN)_6^{4-} + {}^1/_2 S_4O_6^{2-} \qquad (11)$$

strongly catalyzed by citrate stabilized gold colloids. By varying particle size and dimensions, it was found that the reaction rate was surface and not diffusion controlled.[328,329]

Another example of a metal-mediated electron transport is based on $[Pt_3(CO)_6]^{2-}$ clusters and organic liquid membranes. A two-phase system was prepared consisting of a CH_2Cl_2 solution of $[Bu_4N]_2[Pt_3(CO)_6]_{n-1}$ and an aqueous solution of $Fe(CN)_6^{3-}$ (eq 12).

$$n[Pt_3(CO)_6]^{2-}{}_{n-1} + 2[Fe(CN)_6]^{3-} \rightarrow (n-1)[Pt_3(CO)_6]^{2-} + 2[Fe(CN)_6]^{4-} \qquad (12)$$

$$n = 4\text{–}6$$

An overall reduction of ferricyanide by hydroxide ion via transport of electrons and sodium ions across the methylene chloride–water interface and by the reactions in eqs 13 and 14 complete the catalytic cycle.[330]

$$(n-1)[Pt_3(CO)_6]^{2-}{}_n + 2OH^- \rightarrow n[Pt_3(CO)_6]^{2-} + H_2O + {}^1/_2 O_2 \qquad (13)$$

$$[Bu_4N]_2[Pt_3(CO)_6]_n + 2NaOH \rightarrow 2[Pt_3(CO)_6]_n + 2Bu_4N + OH^- \qquad (14)$$

Table 27. Recent Examples of Catalytic Redox Reactions on Colloidal Metal Oxides (Reprinted from Ref 325; Copyright 1991 Marcel Dekker, Inc.)

reaction	catalyst	comments	reaction	catalyst	comments
photochemical O_2 evolution, $S_2O_8^{2-}$ sacrificial acceptor	IrO_2, Co_3O_4, RuO_2, $NiCo_2O_4$, Rh_2O_3, Mn_2O_3	$Ru(bpy)_3$ irrad.; effect of inert oxides support; correlation with support	photooxidation of Cl^-	WO_3	
photochemical and radiolytic O_2 evolution from water	IrO_x	pH-dependent due to ΔG_0, surface and particle changes	azide oxidation	ZnO	
photoevolution of H_2	Pt/TiO_2	pH effect in methanolic solutions. Band gap irrad.	photocatalytic oxidation of HSO_3^-	α-Fe_2O_3	surface complexes implicated as reactive intermediates
water photo-splitting in MV^{2+} aq solution. $\lambda >$ 400 nm	WO_3/M; M = Pd, Pt, Rh	H_2 and O_2 evolution	photoreduction of M^{n+}	TiO_2	selective reduction from Cl^- solution. M^{n+} = Rh(III), Pd(II), Pt(IV), Au(III), Ag^+
H_2 and O_2 evolution	ternary titanates		photoreduction of Ag^+ and NO_3^-	TiO_2	adsorbed propan-2-ol as donor
catalytic and photocatalytic O_2 evolution	various metal oxides/ hydroxides	Model for green plant photosystem II	photomineralization of chlorophenols	TiO_2	langmuir–Hinshelwood kinetics. Hydroquinone intermediate
H_2S photode-composition	RuO_2 on Al_2O_3	CdS excitation. Interparticle electron transfer	photoreduction of Hg(II)	TiO_2	elimination from $HgCl_2$ and CH_3HgCl; dependence pH, MeOH, air metallic Hg identified
photocatalyzed reduction of carbon to CH_3OH, C, HCHO, HCO_2^-	TiO_2/Pt	Cr, Mn doping effect	photodegradation of $CCl_3CH(OH)_2$	TiO_2, ZnO, WO_3	effect pH and H_2O_2
photoreduction of CO_2 to methanol	Cu_2O		photodegradation of surfactants	TiO_2	
photoactivation of CH_4	TiO_2 loaded with MoO_3 and $H_4SiW_{12}O_{40}$	room temp, oxidation to CO	photooxidation of propan-2-ol; mineralization of chlorophenol	N_2O_5 in Bi_2O_3 solid solution	correlation with structure
photocatalytic hydrogenation of C_2H_4	TiO_2 with bimetallic combinations	Pt/Cu combination optimal			band gap irrad.
photoisomerization and hydrogenation of *cis*-butene	TiO_2/Pt	Selectively to ethane	photocatalytic regeneration of NAD(P)H	TiO_2/CdS	implications for enzymatic reactions
			photooxidation of Methyl violet	TiO_2	
			oxidation of alcohols and acids	TiO_2 in pillared clays	quantum size effects on catalytic activity

Photocatalysis

Water Decomposition

Research into converting visible light into alternative energy depends on the use of colloidal catalysts. The basic principles were reviewed[331] for photoelectrochemical cells where light provides the energy for electron transfer. Light absorption by one of the constituents in the system creates an excited state where an electron-hole (e^-h^+) pair forms. In order to utilize light energy effectively, one must achieve charge separation of e^-h^+ due to the short lifetime of the e^-h^+ pairs. When a light-absorbing semiconductor is immersed in solution, charge transfer occurs at the interface. A description of the mechanism of charge separation for a semiconductor in solution is shown in Figure 28.[331]

There are many reports on the use of colloids as either the semiconductor or one or more of the catalyst electron relays. Platinum colloids were produced by radiolysis of aqueous H_2PtCl_6 in acrylamide or NMAM.[332] The colloids were stable and had low poly dispersivity. The colloids were used as redox catalysts for light-induced hydrogen generation from water. In this system Ru-$(bipy)_3^{2+}$ acts as a visible-light-absorbing sensitizer, and interacts with an electron relay agent such as MV^{2+} (eqs 15 and 16). The MV^+ generated in eq 16 can reduce

$$Ru(bipy)_3^{2+} \xrightarrow{h\nu} Ru(bipy)_3^{2+*} \qquad (15)$$

$$Ru(bipy)_3^{2+} + MV^{2+} \rightarrow Ru(bipy)_3^{3+} + MV^+ \qquad (16)$$

water in the presence of a catalyst (eq 17), where the "Pt" species is the colloidal platinum described above.

$$2MV^+ + 2H_2O \xrightarrow{Pt} H_2 + 2OH^- + 2MV^{2+} \qquad (17)$$

The pulse radiolytic method for producing platinum colloid has been employed by other groups.[72,333] In one case,[334] these catalysts have been used for hydrogen production in the presence of Zn porphine complexes.

The stability of the platinum colloid depends on the polymer matrix stabilizer and the method of formation, e.g. the polydispersivity, and these parameters affect catalytic efficiency. The duration and rate of evolution of H_2 was affected by the polymer supports to which

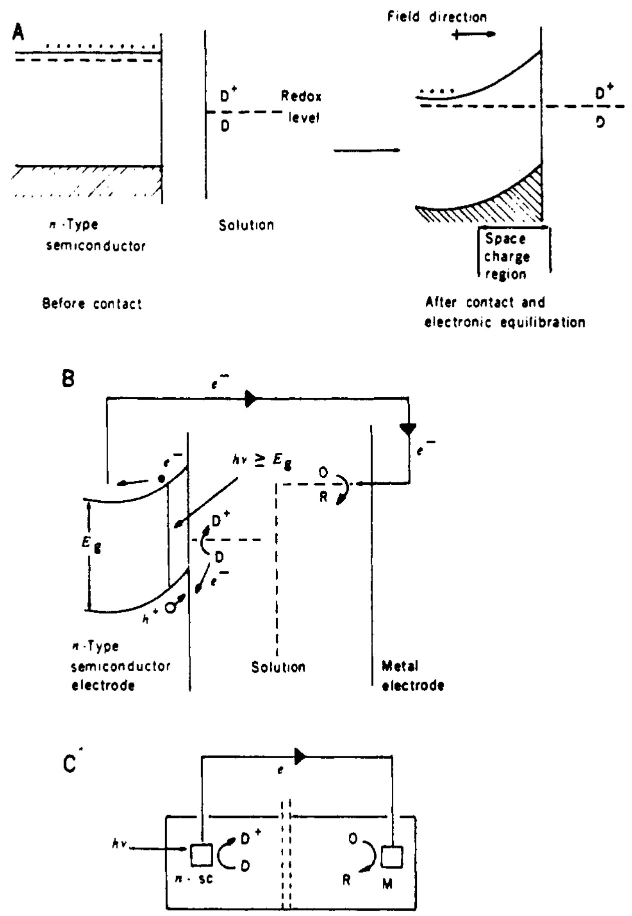
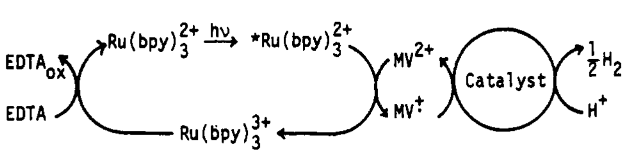


Figure 28. n-Type semiconductor photoelectrochemical cell. (A) Formation of space charge on immersion in solution with redox couple D/D$^+$. (B) Electron flow under irradiation with solution containing species D and O. (C) Cell configuration. (Reprinted from ref 331; copyright 1980 AAAS.)

the colloid is stabilized: NMAM > PVA > PVP-*co*-(diethylamino)ethyl methacrylate ~ poly-2-acetamido-2-methylpropanesulfonic acid > PEG ~ polystyrenesulfonic acid.

Colloidal platinum is obtained by simple water/alcohol reflux of H_2PtCl_6 in the presence of PVA or PVP.[335] The colloids produced had an average diameter of 30 Å and effectively catalyzed light-induced hydrogen evolution from water (eq 18).[335] Note that EDTA is



(18)[335]

used as an electron donor in the system. Hydrogen evolution rates were a function of colloid size, concentration, and pH. Similar results using colloidal platinum and other polymer stabilizers have been reported.[336,337] Colloidal PtO_2 has been employed as a photoredox catalyst as well.[338]

Improvements in the efficiency of hydrogen generation have depended on the stabilizers used for the colloidal metal catalysts. Improvements in the stability of these colloidal systems result in enhanced charge separation and thus more effective catalysts. Polymerized micelles provide better catalyst activity than that obtained with linear polymer stabilizers.[96,98] The efficiency of the colloid-catalyzed hydrogen evolution also depended on the charge of the surfactants in the polymerized micelle, as shown in Table 28. The anionic-stabilized polymerized micelle platinum colloids were generally smaller in size than the corresponding nonionic micelle, e.g 11 Å vs 19 Å for $(CH_2{=}CH(CH_2)_8COO^-Na^+$ vs $(CH_2{=}CH(CH_2)_8COO(CH_2CH_2O)_nCH_3$. The size difference presumably directly affects catalytic activity.

Table 28. Catalytic Activities of Platinum Cluster Catalysts for Photochemical Hydrogen Generation from Water in the System EDTA/Ru(bpy)$_3^{2+}$/MV^{2+}/Pt (Reprinted from Ref 98; Copyright 1988 Marcel Dekker, Inc.)

Pt cluster[a]	protective material
Pt-PC'$_{11}$EO	nonionic polymerized micelle
Pt-MC$_{12}$EO	nonionic monomeric micelle
Pt-PC'$_{11}$N$^+$	cationic polymerized micelle
Pt-MC$_{12}$N$^+$	cationic monomeric micelle
Pt-PC'$_{10}$COO$^-$	anionic polymerized micelle
Pt-MC$_{10}$COO$^-$	anionic monomeric micelle
PT-PVP	nonionic linear polymer
Pt-PAA$^-$	anionic linear polymer

[a] Prepared by a photoreduction method. P = polymerized, M = monomeric.

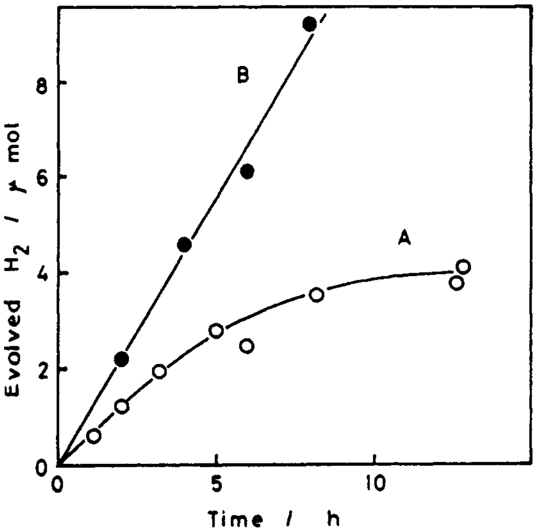


Figure 29. Time dependence of hydrogen evolution with (A) hydrogenase and (B) colloidal Pt. (Reprinted from ref 339; copyright 1981 Elsevier Sequoia S. A.)

The use of a micelle to stabilize platinum colloidal catalysts and induce charge separation is reminiscent of a biological system's electron transfer mechanism. A comparison of hydrogenase to colloidal platinum was made in terms of rate and durability of the catalyst.[339] Synthetic systems are still much less effective than those that have evolved in nature. Hydrogenase was both 500 times more active than platinum and more durable (Figure 29). The platinum-catalyzed system fails due to agglomeration of the platinum colloid. A marriage of artificial and synthetic technology was a study where chloroplasts were infused with colloidal platinum. This mixture was a photoredox catalyst.[340]

Synthetic catalysts for hydrogen evolution are not limited to platinum. One study compared the activity and other properties of a variety of metal colloids generated via the pulse radiolytic method and stabilized

Table 29. Quantum Yields for Hydrogen Formation from the Irradiation (λ_{exc} = 453 nm) of Aqueous Solutions (pH 5) Containing 5.65×10^{-5} M $Ru(bpy)_3^{2+}$, 3×10^{-3} M MV^{2+}, 0.1 M Ethylenediaminetetraacetic Acid, and Various Colloidal Metals (Reprinted from Ref 341; Copyright 1985 Elsevier Sequoia S. A.)

experiment	catalyst	method of preparation	preparation	particle diameter (Å)	metal concentration[a] (M)	$\phi(^1/_2H_2)$[b]
1	Pt	chemical	K_2PtCl_4–PVA	16–1000	1.92×10^{-5}	0.171
2	Pt[c]	chemical	K_2PtCl_4–PVA	16–1000	1.92×10^{-5}	0.105
3	Pt	radiolytic	K_2PtCl_4–PVA	15	2×10^{-5}	0.170
4	Pt[d]	radiolytic	K_2PtCl_4		2×10^{-5}	0.100
5	Ir	radiolytic	H_2IrCl_6–PVA	12	2×10^{-5}	0.173
6	Ir	radiolytic	H_2IrCl_6–PVA	40	2×10^{-5}	0.173
7	Ir	radiolytic	H_2IrCl_6–PVA	<8	2×10^{-5}	0
8	Os	radiolytic	$OsCl_3$–PVA	*e*	5×10^{-5}	0.160
9	Ru	radiolytic	$RuCl_5$–PVA	*e*	6×10^{-5}	0.139
10	Rh	radiolytic	$RhCl_3$–PVA	*e*	4×10^{-5}	0.080
11	Co	radiolytic	$CoSO_4$–PVA	*e*	2×10^{-5}	0.066
12	Ni	radiolytic	$NiSO_4$–PVA	*e*	4×10^{-5}	0.060
13	Pd	radiolytic	$PdCl_2$–PVA	*e*	5×10^{-4}	0.056
14	Ag	radiolytic	$AgNO_3$–PVA	*e*	2×10^{-5}	0.050
15	Au	radiolytic	$HAuCl_4$–PVA	*e*	10^{-4}	0.042
16	Cu	radiolytic	$CuSO_4$–PVA	*e*	10^{-5}–10^{-3}	0
17	Cd	radiolytic	$CdSO_4$–PVA	*e*	10^{-5}–10^{-3}	0
18	Pb	radiolytic	$PbClO_4$–PVA	*e*	10^{-5}–10^{-3}	0

[a] As it is difficult to determine the concentration of the reduced metal precisely, the given optimum concentration can be considered as an approximation. [b] Corrected for light-scattering effects by the colloidal particles. [c] Non-deaerated solution. [d] Without PVA. [e] Sols which do not precipitate and do not give the Tyndall effect (particle size of less than 50 Å).

by PVA (Table 29).[341] It is clear from the data in Table 29 why so much work has been devoted to platinum-colloid systems.

Metal oxide colloids were also examined as catalysts for photochemical production of hydrogen from water.[341] The best catalyst consisted of RuO_2 and IrO_2 codeposited on zeolite, $\Phi(1/2\,H_2) = 0.102$ (cf. Table 29). PtO_2 was less active than colloidal platinum. Other metal colloids investigated included RuO_2, Fe_2O_3, Sm_2O_3, CeO_2, MnO_2, and ZnO. Catalysts which were composed of metals deposited on metal oxides were also described. Particularly effective was Ni–TiO_2.

A variation on the theme of using metals other than platinum was recent use of Pt–Au colloids as catalysts for photochemical H_2 production.[342] One issue addressed by this approach is the propensity of colloidal Pt to catalyze hydrogenation of unsaturated bonds present in the other constituents of the photosystem. The mixed-metal colloids were prepared via pulse radiolysis. The bimetallic system was less effective than a pure platinum system because the particle size of the bimetallic colloid increased with increasing gold content. However, upon prolonged irradiation, the bimetallic system is more effective than the purely platinum counterpart because the Pt–Au colloid is a poor hydrogenation catalyst.

Metal oxides alone or in combination with deposited metals are effective catalysts for photochemical water decomposition. The key work from the 1970s has been briefly reviewed.[343] Highly efficient photosystems could be prepared by combination of colloidal TiO_2 (400-Å diameter) loaded simultaneously with colloidal Pt and RuO_2. Because TiO_2 is transparent to visible light, this photosystem employed rhodamine B as a sensitizer. Several reports detail the mechanism of photoassisted electron transfer in TiO_2 colloids.[210,344,345]

Photocatalysts for water decomposition based on RuO_2 colloids have been studied in detail.[346] Unlike their platinum colloid counterparts, RuO_2 colloids were resistant to the use of polymer stabilizers. Without careful control of ionic strength, RuO_2 colloids were only stable to agglomeration for a few hours. Nevertheless, RuO_2 was an effective photocatalyst for water decomposition.

Photohydrogenation

Clearly a straightforward way to use solar energy is the photochemically driven transformation of organic substrates. Whereas hydrogenation of crucial components of the photosystem was considered deleterious, addition of unsaturated substrates permits useful hydrogenation. A photoredox system was described which contained both EDTA and $Ru(bipy)_3^{2+}$ and colloidal metal catalysts.[347] This system was effective at photohydrogen generation and subsequent hydrogenation of styrene, cyclohexene, cyclohex-2-en-1-one, acrylonitrile, benzyl chloride, prop-2-en-1-ol, cyclohexa-1,3-diene, hex-3-yne, butanol, carbon monoxide, and 1,1-diphenylethene. Alkenes and alkynes were reduced, while carbonyl and nitrile groups were not affected. Several metal colloids were studied where activity followed Pt > Rh ≫ Pd; the colloids were either citrate or PVA stabilized.

Another study of photocatalyzed hydrogenation of unsaturated substrates concerned metal colloids formed via reduction of metal halide salts with H_2 and stabilized with PVA.[348] The photosystem employed $Ru(bipy)_3^{2+}$ as a sensitizer, EDTA as an electron donor and MV as an electron acceptor. Ethylene was cleanly hydrogenated to ethane under photocatalytic conditions in the presence of Pt colloid, but no hydrogenation occurred if either Pt colloid or MV was excluded from the system. Mechanistic experiments support a sequence whereby $MV^{\cdot+}$ reacts with the metal colloid, rather than direct interaction of reduced MV with olefin. Photohydrogenation of acetylene gave a 6:1 product ratio of ethylene and ethane. The relative activity, as measured by quantum yield Φ, was Pd > Pt. However, the highest activity was obtained from colloidal Pt coated with Pd. This active catalyst was prepared by adding $PdCl_2$ to Pt colloid and then bubbling H_2 through the solution.

The above discussed photocatalytic hydrogenation occurred in aqueous solution. A modification of the system employed a water–oil, two-phase system.[349] When undecanol was used, reduction of H_2PtCl_6 resulted in 23 ± 6 Å diameter colloidal particles, while the analogous Pd colloid was 52 ± 6 Å in diameter. Opposite relative activities for Pt and Pd colloids were found for dark vs photocatalyzed hydrogenation of acetylenes. Platinum was more active for photocatalysis than palladium.

Photocatalytic systems are described for other metals and other reduction processes. One example is the photocatalyzed conversion of CO_2 to CH_4 and higher hydrocarbons in the presence of Ru and Os colloids.[350] A photosystem used in this study employed $Ru(bipy)_3^{2+}$ as a photosensitizer, triethanolamine (TEOA) as an electron donor, and one of several electron relay molecules, such as *N,N'*-dimethyl-2,2'-bipyridinium (MQ^{2+}). The Ru and Os colloids were prepared via citrate reduction. Of the corresponding salts, the Ru colloid was 400 Å in diameter whereas the Os colloid was 50 Å in diameter.

Photocatalytic systems for hydrogenation of unsaturated substrates may employ metals deposited on colloidal metal oxide semiconductors.[351] In one study, a photosystem employed a catalyst similar to one described above[343] where Pd, Pt, Cu, and Ni were deposited on TiO_2 powders (300 Å diameter). These metal-coated powders were effective photocatalysts for the hydrogenation of ethylene. An effective catalyst was composed of Cu and Pt codeposited on TiO_2.

Other species deposited on colloidal TiO_2 effectively photocatalyze the hydrogenation of unsaturated substrates.[352] Molybdenum oxides (IV and V oxidation states) interact with trapped electrons on preirradiated TiO_2. The Mo_2 sites are active for catalytic hydrogenation of acetylene to give both ethene and ethane, whereas Mo_3 sites are active for hydrogenation of acetylene to give only ethane.

A large body of work on cluster catalysis uses olefin hydrogenation as a model reaction to test for activity. Some examples of photocatalytic systems have been reported. In one case, the well-known Ru_4 cluster $H_4Ru_4(CO)_{12}$ catalyzes photoinduced hydrogenation of ethylene.[353a,b] The catalyst is thermally active (72 °C), but not at lower temperatures. Irradiation of a solution of $H_4Ru_4(CO)_{12}$ with ethylene (no hydrogen) gives 2 equiv of ethane/mol of cluster, indicating transfer of the cluster's hydrides to the ethene molecules. Circumstantial data support an Ru cluster as the final product. A high turnover rate was found if hydrogen was present during irradiation of ethene in the presence of the Ru_4 cluster. The rate of hydrogenation was retarded by added CO and enhanced with added cluster. After a photochemical hydrogenation run, nearly all of the Ru_4 cluster was recovered intact. Further data supported catalysis via an intact cluster.

A recent application of metal oxide photoinitiated charge transfer mediated by metal oxide colloid was a photoinduced charge transfer between fullerenes (C_{60} and C_{70}) and ZnO colloids.[354] The triplet excited state for fullerenes was characterized by transient absorption measurements, but ZnO clusters generate photoinduced excited states of the fullerene. The ZnO colloids were 20–25 Å in diameter in ethanol. The mechanism of charge transfer is shown in eqs 19a and 19b, where e and h stand for electrons and holes and CB and t stand for "conduction band" or "trapped." Still another application of colloidal metal oxides was suggested by a referee. Colloidal TiO_2 suspensions are photocatalysts for the degradation of chlorinated hydrocarbons in aqueous solution. A brief review of this work has recently appeared.[355]

$$ZnO \xrightarrow{h\nu} ZnO\,(e_{CB}^- + h_{VB}^+) \rightarrow ZnO\,(e_t^- + h_t^+) \quad (19a)^{355}$$

$$ZnO\,(e_{CB}^- \text{ or } e_t^-) + C_{60}\,(\text{or } C_{70}) \rightarrow ZnO + C_{60}^-\,(\text{or } C_{70}^-) \quad (19b)^{355}$$

$$W_{12}^{3-} + Me_2CHOH \xrightarrow{h\nu} W_{12}^{4-} + Me_2\dot{C}OH + H^+$$

$$W_{12}^{4-} + Me_2\dot{C}OH \xrightarrow{h\nu} W_{12}^{5-} + Me_2CO + H^+$$

$$W_{12}^{5-} + W_{12}^{3-} \rightarrow 2W_{12}^{4-}$$

followed by

$$2W_{12}^{4-} + {}^1/_2O_2 + 2H^+ \rightarrow 2W_{12}^{3-} + H_2O$$

$$W_{12}^{5-} + {}^1/_2O_2 + 2H^+ \rightarrow W_{12}^{3-} + H_2O$$

where $W_{12} \equiv PW_{12}O_{40}$

$$Me_2CHOH + {}^1/_2O_2 \xrightarrow{h\nu} Me_2CO + H_2O$$

Figure 30. Relevant equations for the photocatalyzed oxidation of alcohols to aldehydes and ketones in the presence of polyoxometalates. (Reprinted from ref 356; copyright 1985 the American Chemical Society.)

Polyoxometallates are soluble models of metal surfaces and active catalysts and catalyst support in their own right. These clusters catalyze the photooxidation of alcohols to the corresponding aldehydes or ketones according to the equations of Figure 30.[356a] The cluster $H_3PW_{12}O_{40}\cdot 6H_2O$[356a] and other polyoxometalates[356b–d] appear to remain intact during photocatalyzed oxidations of a variety of organic substrates.

Metal semiconductor colloids other than oxides can also act as catalysts. One report describes the catalytic activity of colloidal metal sulfides for the photochemical decomposition of H_2S.[357]

Water Activation

Colloids and clusters catalyze the activation of water. As discussed in the previous section, photocatalytic decomposition of water is key to efficient use of solar energy. Many systems employ catalysts for oxidation of water (eq 20).[358] Useful catalysts for the reaction in eq 20 include colloids of Co(III) and Fe(III) hydroxides prepared by rapid addition of, for example, $Fe(NO_3)_3$ to 1–2 M NaOH solutions containing PVA. Small-angle scattering measurements showed slightly stretched-shaped sols with an average diameter of 20–30 Å. The O_2 formation rate was a function of sol particle size; large particles generated O_2 at a slower rate than smaller catalysts.[358] Earlier work claimed RuO_2 colloids as active catalysts for water oxidation,[359] but later work[358] found RuO_2 colloids to be rather poor catalysts. RuO_2 colloids had maximum catalytic activity at pH 9.[359]

$$4Ru(bipy)_3^{3+} + 2H_2O \rightarrow 4Ru(bipy)_3^{2+} + O_2 + 4H^+ \quad (20)$$

In one interesting study, colloidal Ir was prepared via radiolytic reduction of hexachloroiridate in alcohol containing the polymer carbomer 20M. Solutions containing the 10–20 Å diameter particles slowly turn blue at pH 7 in air and form IrO_2 colloids. The change from Ir to IrO_2 can also be followed with absorption spectroscopy, with the IrO_2 having a maximum absorption at 580 nm. The Ir colloids catalyze formation of H_2 from water. If the experiment was carried out in air, H_2 formed after an induction period. Presumably the IrO_2 generated in air is rereduced to Ir via ketyl radicals present under the experimental conditions. The IrO_2 colloids catalyze reduction of Ce^{4+} ions via complex kinetics with formation of a small yield of O_2. The activity of IrO_2 was similar to RuO_2, which as stated above, had poor activity.[182]

Polymer-protected copper colloids catalyze hydration of nitriles. Black or reddish dark brown colloidal copper solutions were prepared by borohydride reduction of copper sulfate in the presence of various protecting polymers. The hydration of nitriles was catalyzed by the colloidal copper.[360] Acrylonitrile was converted to acrylamide in about 25% yield in the presence of PVA-protected copper colloid. The selectivity was 100%.[73,360]

A short summary of metal-cluster activation of water has been published.[351] Anionic platinum carbonyl clusters catalyze oxidation of water. The reactions in eqs 21 and 22 are relevant to the observed catalysis.

$$(n-1)[\{Pt_3(CO)_6\}_n]^{2-} + H_2 \rightarrow n[\{Pt_3(CO)_6\}_{n-1}]^{2-} + 2H^+ \quad (21)$$

$$n[\{Pt_3(CO)_6\}_{n-1}]^{2-} + 2H^+ + {}^1/_2O_2 \rightarrow (n-1)[\{Pt_3(CO)_6\}_n]^{2-} + H_2O \quad (22)$$

Water oxidation (the reverse of eq 22) can be coupled to the reduction of *p*-benzoquinone to benzene-1,4-diol conversion to create a catalytic cycle in the presence of $[n\text{-}Bu_4N]_2[Pt_{12}(CO)_{24}]$.[361]

The water–gas shift (WGS) reaction, eq 23, is another

$$H_2O + CO \xrightarrow{\text{catalyst}} H_2 + CO_2 \quad (23)$$

example of metal-catalyzed water activation. A summary has appeared for metal clusters that catalyzes the WGS reaction.[239] The hydrogen produced in eq 23 can be used in a hydrogenolysis reaction. Quinolines and isoquinolines were hydrogenated under WGS conditions in the presence of $Rh_6(CO)_{16}$. Table 30 gives results for a variety of metal clusters. Note that the two mononuclear compounds in the table were inactive.[254] The $Rh_6(CO)_{16}$ has been reported elsewhere as a WGS catalyst in the presence of ethylene diamine[270] and details of the oxygen atom exchange between CO_2 and H_2O have been described.[362]

Table 30. Catalytic Activity of Various Metal Complexes for the Hydrogenation of 1[a] (Reprinted from Ref 254; Copyright 1989 the Chemical Society of Japan)

entry	catalyst	amount (mol %)	convn[b] (%)	yield (%)
1	$Rh_6(CO)_{16}$	0.81	100	97
2	$Rh_4(CO)_{12}$	1.2	80	75
3	$[Rh(COD)Cl]_2$	2.4	65	62
4	$Ru_3(CO)_{12}$	1.6	70	65
5	$W(CO)_6$	3.3	0	0
6	$Fe(CO)_5$	3.3	0	0

[a] A mixture of quinoline (2.31 mmol), water (0.5 mL), and catalyst in 2-methoxyethanol (2 mL) was heated at 150 °C for 12 h under the pressure of CO (56 kg cm^{-2}). [b] Determined by GLC analysis.

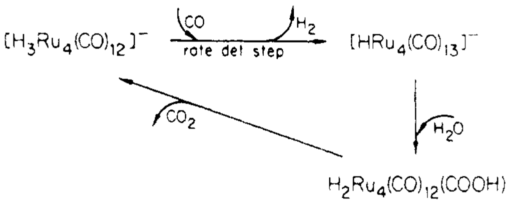


Figure 31. Proposed catalytic cycle for the water–gas shift reaction catalyzed by $[H_3Ru_4(CO)_{12}]^-$. (Reprinted from ref 363; copyright 1982 the American Chemical Society.)

Anionic ruthenium carbonyl clusters catalyze the WGS reaction. Mechanistic data for the reaction strongly implicates intact cluster intermediates without evidence of mononuclear compounds.[363] Figure 31 shows the proposed cycle for this reaction.

Oxidation

Colloids catalyze oxidations. Reactions in organic and aqueous solution, mediated by permanganate, generate brown-yellow manganese species. As shown in Table 31, a large number of unsaturated organic compounds react with methyltributylammonium permanganate to give a reduced manganese species of average oxidation state IV.[364] Several studies on permanganate oxidation of olefins and other organic substrates have shown that the manganese(IV) species is colloidal MnO_2.[365–369]

Table 31. Data for the Reduction of Methyltributylammonium Permanganate by Several Olefinic Compounds in Methylene Chloride (Reprinted from Ref 364; Copyright 1985 the National Research Council of Canada)

compound	oxidation state	isosbestic point (nm)	slope[b]
butyl vinyl ether	3.97	488	*c*
cyclododecene	4.05	483	*c*
cyclooctene	3.93	482	4.70
1-decene	4.05	485	5.04
cis-2-decene	3.95	483	5.04
2,3-dihydrofuran	4.02	481	4.11
2,3-dimethyl-2-butene	3.94	482	4.70
1-eicosene	3.98	485	4.93
trans-2-heptene	4.02	486	*c*
1,5-hexadiene	3.99	484	5.06
isoprene	3.90	483	5.21
β-methoxystyrene	4.05	488	*c*
2-methyl-1-butene	4.05	485	*c*
2-methyl-2-butene	3.99	483	4.55
methyl cinnamate	4.01	483	4.09
cis-4-methyl-2-pentene	4.03	488	*c*
α-methylstyrene	4.00	484	5.11
β-methylstyrene	3.95	484	4.72
1-octene	4.02	485	4.82
trans-2-octene	3.99	484	5.00
2,2,4,6,6-pentamethyl-3-heptene	4.02	485	*c*
trans-4-phenyl-3-buten-2-one	3.90	484	4.42
trans-1-phenyl-1-pentene	3.95	484	*c*
cis-stilbene	4.03	485	*c*
styrene	4.03	484	4.49
1-tetradecene	4.03	484	3.85

[a] Oxidation state of the product. [b] Slope for plots of −log (absorbance) vs log λ. [c] Precipitation occurred.

Table 32. Oxidations with Colloidal Catalysts (Reprinted from Ref 373; Copyright 1992 American Chemical Society)

reaction	catalyst[a]	support[b]
$CH_3(CH_2)_9SH + O_2 \rightarrow [CH_3(CH_2)_9S]_2$	CoPcTS	SCL
$HOCH_2CH_2SH + O_2 \rightarrow (HOCH_2CH_2S)_2$	CoPcTS	SCL, IEL, silica
2,6-di-*tert*-butylphenol + $O_2 \rightarrow$ 2,6,2′,6′-tetra-*tert*-butyl-1,4-diphenoquinone	CoPcTS	IEL
styrene + NaOCl → styrene oxide	$Mn^{III}(Cl)TPPCl_8TS$	IEL
alkenes + NaOCl → epoxides and diols	$Mn^{III}(Cl)TPPCl_8TS$	IEL
alkenes + $KHSO_5 \rightarrow$ epoxides and diols	$Mn^{III}(Cl)TPPCl_8TS$	IEL
cyclooctene + $H_2O_2 \rightarrow$ cyclooctene oxide	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	IEL
tetrahydronaphthalene (tetralin) + $O_2 \rightarrow$ α-tetrol + α-tetralone	$Co^{II}(pyr)_6$	ASL, ACL

[a] CoPcTs = cobalt phthalocyaninetetrasulfonate. $Mn^{III}(Cl)TPPCl_8TS$ = chloromanganese(III) *meso*-tetrakis(2,6-dichlorophenyl)porphyrintetrasulfonate. $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ forms unidentified oxomolybdate anions in hydrogen peroxide. $Co^{II}(pyr)_6$ = Co^{II} in the presence of at least 6 molar equiv of pyridine. [b] SCL = cationic surface charged latex. IEL = cationic ion exchange latex. ASL = anionic sulfonate latex. ACL = anionic carboxylate latex.

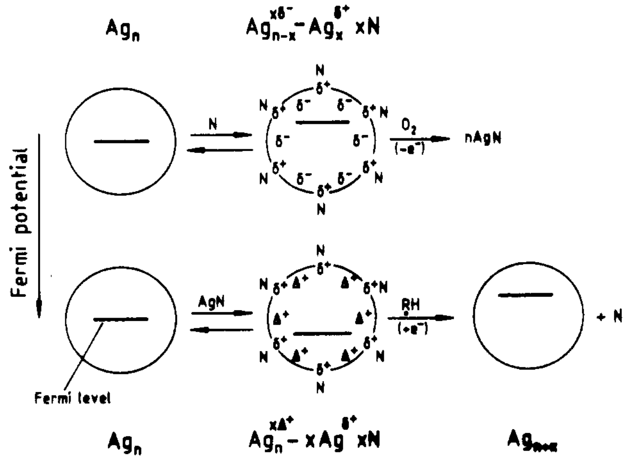


Figure 32. Top: surface complexation (preoxidation) by a nucleophilic reagent N and final oxidation of the silver particle by oxygen. Bottom: chemisorption of a complex AgN and final reduction of the silver ions in chemisorbed AgN by excess electrons deposited by reducing radicals. (Reprinted from ref 371; copyright 1991 the American Chemical Society.)

A second example of a metal oxide colloid catalyst was discussed above for the IrO_2 colloid catalyzed oxidation of water.[182] A polyoxoanion of niobium, $SiW_9(NbO_2)_3O_{37}{}^{7-}$, is the catalyst precursor for allylic epoxidations with H_2O_2. The active catalyst is believed to be a polyoxoanion fragment.[370]

$Rh_6(CO)_{16}$ catalyzes conversion of CO to CO_2 and PPh_3 to O = PPh_3 in the presence of O_2. The proposed mechanism, based on IR data, shows catalysis via multinuclear species.[362]

An important oxidation reaction is that for silver colloids. The mechanism in Figure 32 shows silver particles with nucleophilic absorbates, N. The silver particles, with the absorbates on their surface, are very reactive toward O_2, which picks up the excess negative charge (perhaps by formation of O_2^- or O_2^{2-}), thus allowing further complexation of surface atoms until the whole particle is oxidized. In addition to the oxygen-catalyzed reaction, oxidation of silver particles in the absence of air occurs with electron acceptors such as nitrobenzene, methyl viologen, and hexacyanoferrate and nucleophiles (N) such as CN^- and SH^-.[371]

Thermal decomposition of $Fe_y(CO)_x$ or $(alkyl)_xFe_y(CO)_z$ forms stable iron colloids in the presence of protecting polymers. These polymer-protected iron colloids are catalysts for oxidative coupling.[67] Aqueous platinum colloids, stabilized by citrate, catalyze the oxidation of tetrathiafulvalene (TTF) to TTF^+.[372]

An area that falls within the realm of this review is catalysts supported on polymer colloids. Polystyrene latexes were prepared via cationic polymerization using surfactant catalysts such as hexadecyltrimethylammonium chloride. Latexes were prepared with a variety of metal complexes. Table 32 shows a number of oxidation reactions catalyzed by colloids.[100,373]

Electrochemistry and Electroless Metal Deposition

Clusters and colloids are important in the areas of electrochemistry and electroless plating applications. Metalization of substrates via chemical reduction has been known for over 80 years.[374] Electrochemical reduction of benzene is catalyzed by ruthenium colloids. The Ru colloids are generated by decomposition of a ruthenium acid sulfite complex. The ruthenium colloid was more efficient than a corresponding platinum colloid.[375]

Electroless metal deposition is the process for chemical deposition of a metal coating on a substrate in the absence of an external electrical source. The deposition of copper, nickel, palladium, gold, or cobalt from aqueous solutions is catalyzed by colloidal palladium, gold, or platinum. In a typical procedure, a palladium colloid solution is prepared from $PdCl_2$, $SnCl_2$, and HCl(aq). A substrate is then immersed in the palladium colloid solution, leaving a small amount of Pd colloid behind. Deposition of such metals as copper is accomplished by immersion in a solution composed of formaldehyde and a salt mixture.[376]

Minor improvements have been described for the adherence of the metal formed by electroless deposition. A typical copper plating bath includes $CuSO_4$, propylenediaminetetraacetic acid, basic formaldehyde, and sodium cyanide.[377]

The active catalyst for electroless deposition is believed to be a tin–palladium colloid. Catalytic performance is improved by using colloids with smaller diameters.[378] Colloidal palladium catalysts, free of tin, can be prepared with diameters <500 Å. Palladium salts are reduced with dimethylaminoborane, sodium borohydride, ascorbic acid, formic acid, and formaldehyde. The colloid is stabilized against agglomeration with polymers such as cellulose, polyacrylamides, and PVP.[379]

More recent work with mixed Pd–Sn colloids concluded that higher activity was achieved with larger colloids. So-called accelerators, such as ammonium tetrafluoroborate, cause coagulation of small particles with concomitant increase in catalytic activity.[172,380a,b,381] Improvements have been made in photoselective catalysis of electroless copper deposition with palladium catalysts. The palladium metal catalysts are generated from Pd^{2+} via photoreduction of potassium iron(III) oxalate.[381a] Further improvement in the deposition of thin Pd films from baths of palladium colloid precursors have recently been described.

A process similar to electroless plating is the silver-based photographic process. Silver clusters reach a critical size and then catalyze reduction of silver halide to silver metal.[382]

Ammonia Synthesis and Related Nitrogen Chemistry

The ruthenium carbonyl clusters $Ru_3(CO)_{12}$, $[(HRu_3(CO)_{11}]^-$, and $[(H_3Ru_4(CO)_{12}]^-$ catalyze carbonylation of cyclic amines to give formamides. For example, piperidine reacts with CO to give *N*-formylpiperidine. The carbamoyl cluster $(\mu_2\text{-H})Ru_3(CO)_{10}(\mu_2,\eta^2\text{-OCNR}_2)$ was isolated from the reaction mixture. A mechanism based on cluster intermediates was proposed[383] (Figure 33).

Other studies employ a variety of catalysts, including clusters in amide synthesis, but the actual catalyst is not known. Both RuO_2 and $Ru_3(CO)_{12}$ catalyze the reaction between carbon monoxide, hydrogen, and ammonia to give formamide, *N*-methylformamide, *N*,*N*-dimethylformamide, and trimethylamine.[384] The formation of dimethylformamide from carbon dioxide, hydrogen, and dimethylamine is catalyzed by $Pt_2(\mu_2\text{-}Ph_2PCH_2PPh_2)_3$.[385] Finally, formamides were prepared from carbon monoxide, hydrogen, and ammonia in the presence of $Ru_3(CO)_{12}$. A monomeric ruthenium complex was observed in one case but the nature of the actual catalyst was not investigated.[386]

Ammonia synthesis is well-known to rely on iron-based catalysts. One study clearly showed improved catalyst performance when the catalysts were prepared from colloidal intermediates. While the final catalyst was indeed heterogeneous, the origin of the improved catalytic activity was the high surface area of the colloidal precursor.[387] Ammonia was prepared from catalysts derived from dual colloid, mixed transition metal crystallites. The crystallites had a diameter of from 25 to 500 Å. One composition was prepared by refluxing an aqueous solution of $Al(NO_3)_3$, $Mg(NO_3)_2$, $Co(NO_3)_2$, and $K_4Fe(CN)_6$. The reaction of the resultant solid with hydrogen, nitrogen, and ammonia produced 567 g of NH_3/L of catalyst/h.[388,389]

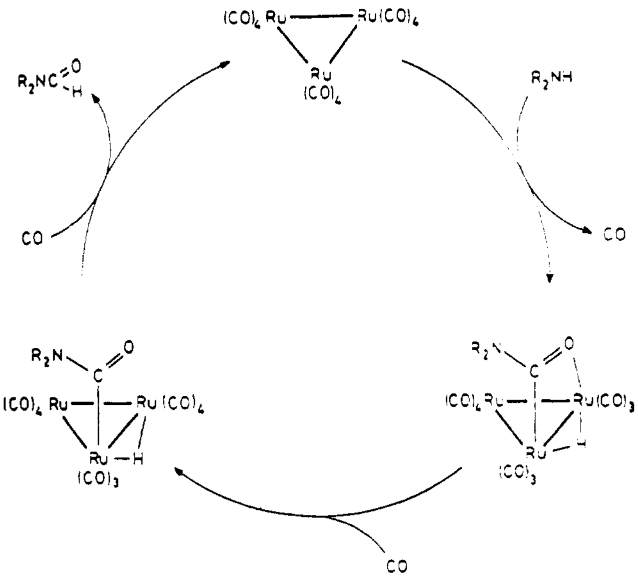


Figure 33. Proposed catalytic cycle for the carbonylation of a cyclic amine with $Ru_3(CO)_{12}$ as the catalyst. (Reprinted from ref 383; copyright 1989 Elsevier Sequoia S. A.)

Table 33. Extent of Formation of Mixed Alkyl Amines from Catalytic Alkyl Exchange between Et_3N and Pr_3N[a,b] (Reprinted from Ref 158b; Copyright 1985 Elsevier Sequoia S. A.)

		catalyst				
product	*T* (°C)	$Rh_6(CO)_{16}$	$Ir_4(CO)_{12}$	$Ru_3(CO)_{12}$	$Os_3(CO)_{12}$	Pd black
Et_2NPr	125	<0.1	1.2	8.9	6.2	
$EtNPr_2$	125	<0.1	2.2	11.0	7.8	
Et_2NPr[c]	150	0.2	6.2	22.8	26.7	1.6[d]
$EtNPr_2$[c]	150	0.6	7.1	25.6	28.4	1.6[d]

[a] The numerical values correspond to (mol mixed amine)/(total mol amine) × 100 and are reproducible to ±5% of the indicated value. Essentially all nitrogen is recovered as tertiary amines. [b] Reaction conditions require heating a mixture of Et_3N (14 mmol) and Pr_3N (14 mmol), 0.1 mL of H_2O, and 0.05 mmol of catalyst under 100 psi of N_2 at 125 °C for 3 h. [c] 0.1 mmol of catalyst. [d] 0.75 mmol of catalyst, 20 h reaction time.

Hydrodenitrogenation (eq 24) is catalyzed by a large number of metal carbonyl clusters. Several clusters

$$R_3N + R'_3N \rightarrow R_2NR' + R'_2NR \qquad (24)$$

successfully model well-known, corresponding heterogeneous reactions. For example, for the catalyzed exchange between Et_3N and Pr_3N, the activity of several clusters is compared to each other and Pd black (Table 33).[158b]

Miscellaneous

Clusters and colloids catalyze a few other reactions not covered above. Platinum colloids are reactive catalysts for hydrogen peroxide decomposition, whereas platinum ions are inactive. A high turnover number was found for colloids with a diameter of 32 Å, but particles with a diameter <16 Å were not active. Alloying platinum with gold or selectively poisoning it with mercuric chloride decreased catalytic activity.[390]

Stoichiometric hydrodesulfurization steps are observed with clusters such as $Cp_2Mo_2Co_2S_3(CO)_4$. For example, the molybdenum–cobalt cluster reacts with thiophene to give $Cp_2Mo_2Co_2S_4(CO)_2$, the sulfur being extracted from thiophene. Catalytic hydrodesulfurization was accomplished by depositing clusters on metal oxide supports.[391]

Metal colloids are utilized in quasicatalytic applications such as xerographic developing material or as ablative optical recording media.[66,67,299]

The cluster $Rh_6(CO)_{16}$ catalyzes the cyclopropanation reaction between ethyl diazoacetate and alkenes. The cluster more effectively catalyzes these reactions than does mononuclear palladium or copper catalysts. Under an atmosphere of CO, the rhodium cluster was "recovered" quantitatively intact.[391]

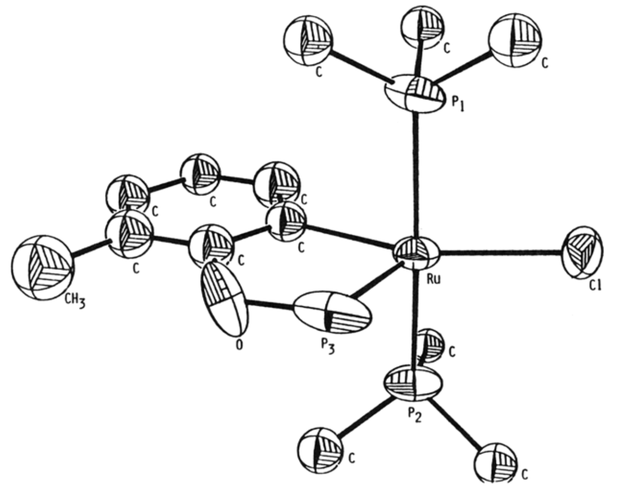


Figure 34. Highly active ruthenium olefin hydrogenation catalyst. (Reprinted from ref 166; copyright 1986 the American Chemical Society.)

Cluster and Colloid Surprise

Catalysis via metal colloids has featured prominently in the work of this author. However, in the two areas where colloids have played a role, hydrogenation and hydrosilylation, the presence of colloids was unanticipated. The ruthenium complex in Figure 34 was an effective hydrogenation catalyst for a variety of substrates, comparable in activity to Wilkinson's complex. When the catalyst was exposed to air, an increase in rate and decrease in selectivity was noted. Some of the methods for distinguishing mononuclear from cluster/colloid catalysts were applied to this system. Mercury had no effect on olefin hydrogenation carried out in the absence of air, but olefin hydrogenations catalyzed by the complex in Figure 34 were inhibited by mercury if air was present. The results with mercury suggested that the hydrogenation catalysis in the presence of air was mediated by colloids.[166]

The ruthenium complex in Figure 34 was a selective catalyst for hydrogenation of 1,5,9-cyclooctatetraene in the absence of air; a mixture of cyclooctadienes and cyclooctenes was formed but no cyclooctane was produced. If the reaction was repeated in the presence of air, 18% yield of cyclooctane was noted. A second example of the difference in hydrogenation selectivity was in the hydrogenation of carvone. The ruthenium complex in Figure 34 was a selective catalyst for the hydrogenation of carvone to dihydrocarvone. These results were indicative of homogeneous catalysis with low nuclearity species.[9,392] The hydrogenation of carvone in the presence of air resulted in complete hydrogenation of the substrate, consistent with colloid catalysis. Formation of ruthenium colloids in the hydrogenation reaction with air present was supported by light scattering and the observation of $O{=}PPh_3$ in the reaction solution.[166]

A study reported polymer-supported rhodium and ruthenium compounds used as precursors for hydrogenation catalysts. The metal compounds were bound to the cross-linked polymer via phosphine linkages. Catalytic activity was effected by method of preparation and oxygen concentration. The reaction also had an induction period under some conditions. These results may be explained by the sequence described above for the ruthenium complex in Figure 34, e.g. colloid formation explaining the induction period and oxygen effects.[393]

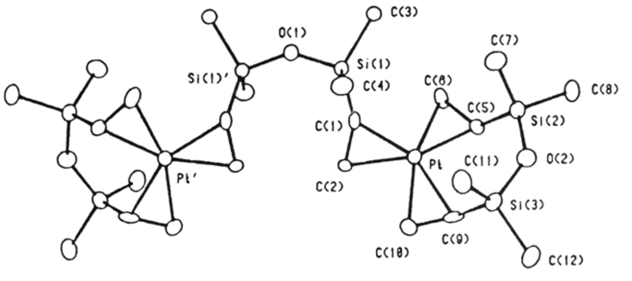


Figure 35. So-called Karstedt's catalyst, prepared by reaction of H_2PtCl_6 + $(H_2C{=}CHSiMe_2)_2O$. (Reprinted from ref 394; copyright 1991 VCH Verlagsgesellschaft.)

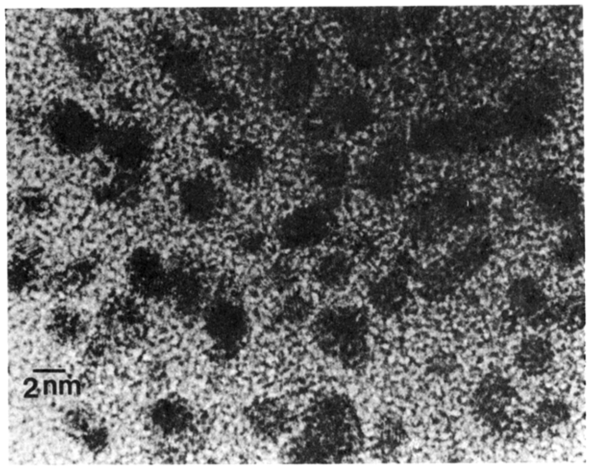


Figure 36. HREM of 20 Å diameter platinum crystallites formed from reaction of $Me_2(EtO)SiH$ + $PtCl_4$. (Reprinted from ref 51; copyright 1989 the American Chemical Society.)

This author has also published extensively about the presence/formation of platinum[56–58,119,309,311] and rhodium[59,312,313] colloids in the hydrosilylation reaction. In an attempt to observe a platinum intermediate from the reaction of an Si–H-containing compound and a platinum complex, colloidal platinum species were observed by TEM from actual solutions from platinum-catalyzed hydrosilylation reactions. The reaction of simple platinum salts such as $PtCl_4$ as well as Pt(0) compounds such as Karstedt's catalyst[393] (Figure 35[394] with Si–H-containing compounds results in colloid formation.[51] For example, the combination of $PtCl_4$ and $Me_2(EtO)SiH$ results in the colloid showed in the TEM in Figure 36. This type of colloid was also observed in a solution from an actual hydrosilylation reaction catalyzed by Karstedt's catalyst.[313]

A number of results in the literature may be explained by invoking colloid formation. Hydrogenation of olefins was catalyzed by ethanol solutions of platinum group metals containing a variety of Si–H-containing compounds.[395] When solutions of platinum group metals are combined with Si–H compounds, colloids form.[51] These solutions catalyzed hydrogenation with a selectivity that suggested colloidal catalysts. For example, a solution derived from $PtCl_4$ and $ClSiH_3$ catalyzed hydrogenation of nitrobenzene to aniline.[395] Recall that hydrogenation of nitrobenzene is indicative of hetergeneous catalysts.[247,288]

Another report described acceleration of hydrosilylation where the catalyst was prepared via reaction of

H_2PtCl_6 with Si–H-containing compounds.[314] Again, it is now known that the reaction of chloroplatinic acid with silicon hydrides results in colloid formation.[51] In yet another publication, $(PPh_3)_2Pt(H_2C{=}CH_2)$ was shown to catalyze formation of HPhMeSi–SiMePhH from reaction with $PhMeSiH_2$. Several other platinum, rhodium, palladium, and iridium complexes catalyze production of Si–Si bonds. Colloids are suspected by the author.[396]

Formation of palladium metal and hydrogen occurs when $(EtO)_3SiH$ contacts palladium acetate in water.[397] The Pd metal was previously observed under similar conditions.[51] The palladium metal is finely dispersed in a polysiloxane matrix, which acts as a highly chemoselective and stereoselective hydrogenation catalyst at room temperature.[397,398]

The investigations of the true nature of the catalytic species in other systems have found colloids and clusters. The permanganate oxidation catalyst system gave colloidal MnO_2 as described above.[364–368,399] The palladium acetate oxidation of olefins leads to formation of the giant Pd clusters.[49,400] One study discussed the copper-mediated Ullman synthesis of triaryl amines from three diverse copper sources: Cu metal and Cu^+ and Cu^{2+} salts. Direct and indirect evidence point to a single, soluble copper source.[401] Given the uncertain nature of the composition of the copper catalyst, a copper cluster or colloid could be the active catalytic species.

Conclusions

A recent publication states, "Larger cluster compounds are continuously being synthesized so that the field of cluster synthesis is merging seamlessly with that of ligand-stabilized colloid chemistry".[108]

This quote summarizes well the thesis of the early part of this review. Clusters contain ≥2 metal atoms and may contain hundreds of atoms. Large clusters have dimensions which overlap with those usually attributed to small colloids. Modern definitions of clusters and colloids may include the following: A colloid is a cluster where the exact identity of the surface atoms is not well-known. A cluster is a discrete molecule with metal–metal bonds where ligands are well-defined. When the surface structure of a colloid is determined, it becomes a cluster. Fullerenes may in fact be considered colloidal carbon if one considers the initial fullerene soot in its entirety. The isolated compounds, C_{60}, C_{70}, etc., are clusters; the continuum of clusters is the colloidal mixture.

The onset of various metallic properties begin for clusters of small size (≥10 atoms). This early onset to metallic property demonstrates the overlap in defining large clusters and small colloids.[402]

Several reviews concluded that few if any reactions were catalyzed by clusters. This review has first addressed the techniques used to determine the nature of the catalytic species (mononuclear vs cluster). Many examples of cluster (and colloid) catalysis are given for a variety of different reaction types. Clusters may not be models for metal surface or heterogeneous catalysis, but they display unique catalytic properties. Future work will center on improved methods for determining the nature of the active catalyst and synthetic techniques for preparing, characterizing, and isolating giant clusters.

Abbreviations

PVA	polyvinyl alcohol
HREM	high-resolution electron microscopy
TEM	transmission electron microscopy
Phen	1,10-phenanthroline
SAXS	small-angle X-ray scattering
EXAFS	extended X-ray absorption fine structure
IR	infrared
ED	electron diffraction
DIOP	2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane
STEM	scanning transmission electron microscopy
PVP	(polyvinyl pyrrolidone)
NMR	nuclear magnetic resonance
UV–VIS	ultraviolet–visible
DOS	density of states
TF	turnover frequency
PMVE	polymethylvinyl ether
PEG	polyethylene glycol
CMC	critical miscellar concentration
CFC	critical floculation temperature
CIR	cylindrical internal reflectance spectroscopy
DMPE	1,2-bis(dimethylphosphino)ethane
DPPM	1,2-bis(diphenylphosphino)methane
DCT	dibenzocyclooctatetraene
BIPY	2,2′-bipyridine
NMAM	*N*-methylolacrylamide
EDTA	ethylenediaminetetraacetic acid
MV	methyl viologen

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