

## 9

# Homogeneous Hydrogenation: Colloids – Hydrogenation with Noble Metal Nanoparticles

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### 9.1

#### Introduction

Today, metal nanoparticle science is a strategic research area in material development due to their particular physical and chemical properties. Catalysis is a traditional application of metal nanoparticles, but they also find application in diverse fields such as photochemistry, electronics, optics or magnetism [1, 2]. Metal nanocatalysts, defined as particles between 1 and 10 nm in size, can be obtained by a variety of methods according to the “organic” or “aqueous” nature of the media and the stabilizers used: polymers, ligands or surfactants [3]. During the past five years, the use of nanoparticles in this active research area has received increased attention since some homogeneous catalysts have been shown to be “nanoheterogeneous” [4–6]. Since that time, modern methods to distinguish the true nature of the catalysts have been described. From today onwards, soluble noble metal nanoparticles are to be considered as an unavoidable family of catalysts for hydrogenation under mild conditions at the border between homogeneous and heterogeneous chemistry. This chapter reviews recent progress in the hydrogenation of unsaturated compounds by noble metal nanoparticles in various liquid media.

### 9.2

#### Concepts

In materials chemistry, nanoparticles of noble metals are an original family of compounds. Well-defined in terms of their size, structure and composition, zero-valent transition-metal colloids provide considerable current interest in a variety of applications. Here, the main interest is their application in catalysis. Zerovalent nanocatalysts can be generated in various media (aqueous, organic, or mixture) from two strategic approaches according to the nature of the precursor, namely: (i) mild chemical reduction of transition-metal salt solutions; and (ii) metal atom

extrusion starting from organometallic compounds able to decompose in solution under mild conditions [7]. To date, the key goal is the reproducible synthesis of nanoparticles in opposition to larger ones (nanopowders) and bulk materials. Consequently, nanostructured particles should have at least: (i) a specific size (1–10 nm); (ii) a well-defined surface composition; (iii) constant properties related to reproducible syntheses; and (iv) be isolable and redissolvable. In this respect, several synthetic methods have been described, including:

- chemical or electrochemical reduction;
- thermal, photochemical or sonochemical decomposition; and
- metal vapor synthesis.

Whichever method is followed, a protective agent able to induce a repulsive force opposed to the van der Waals forces is generally necessary to prevent agglomeration of the formed particles and their coalescence into bulk material. Since aggregation leads to the loss of the properties associated with the colloidal state, stabilization of metallic colloids – and therefore the means to preserve their finely dispersed state – is a crucial aspect for consideration during their synthesis.

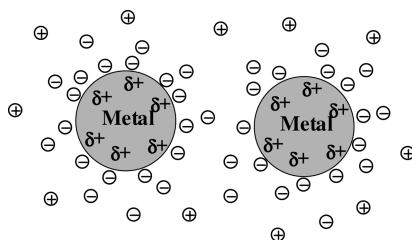
The stabilization mechanisms of colloidal materials have been described in Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [8, 9]. Colloids stabilization is usually discussed in terms of two main categories, namely charge stabilization and steric stabilization.

### 9.2.1

#### Electrostatic Stabilization

Various anionic compounds such as halides, carboxylates or polyoxoanions, generally dissolved in aqueous solution, can establish electrostatic stabilization. Adsorption of these compounds onto the metallic surface and the associated counterions necessary for charge balance produces an electrical double-layer around the particles (Scheme 9.1). The result is a coulombic repulsion between the particles. At short interparticle distances, if the electric potential associated with the double layer is sufficiently high, repulsive forces opposed to the van der Waals forces will be significant to prevent particle aggregation.

Colloidal suspensions stabilized by electrostatic repulsion are highly sensitive to any phenomenon able to disrupt the double layer, such as ionic strength or thermal motion.



**Scheme 9.1** Schematic representation of electrostatic stabilization: a coulombic repulsion between metal colloidal particles.

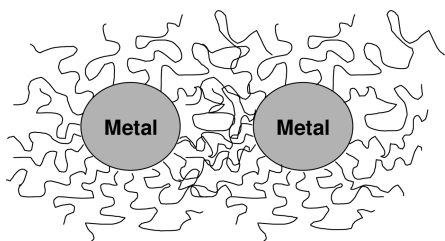
## 9.2.2

**Steric Stabilization**

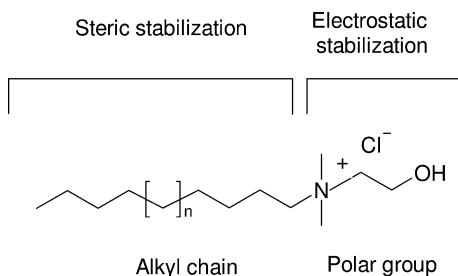
Nanoparticulate metal colloids can also be prevented from agglomeration by using protecting macromolecules such as polymers or oligomers [10, 11] or related stabilizers such as cyclodextrins [12] or cellulose derivatives [13]. The adsorption of these molecules at the surface of the particles provides a protective layer. In the interparticle space, the sterical environment of the adsorbed macromolecules reduces their mobility (Scheme 9.2). The result is an osmotic repulsion to restore the equilibrium by diluting the macromolecules, thereby separating the particles. By contrast with electrostatic stabilization, which is mainly used in aqueous media, steric stabilization can be used in either an organic or aqueous phase. Nevertheless, the length and/or nature of the adsorbed macromolecules can influence the thickness of the protective layer and thus modify the stability of the colloidal metal particles.

The electrostatic and steric effects can be combined to stabilize nanoparticles in solution. This type of stabilization is generally provided by means of ionic surfactants such as alkylammonium cations (Scheme 9.3). These compounds bear both a polar head group which is able to generate an electrical double layer, and a lipophilic side chain which is able to provide steric repulsion [14, 15].

Electrosteric stabilization can be also obtained from the couple ammonium ( $\text{Bu}_4\text{N}^+$ )/polyoxoanion ( $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{2-}$ ). The significant steric repulsion of the bulky  $\text{Bu}_4\text{N}^+$  countercation, when associated with the highly charged polyoxoanion (coulombic repulsion), provides efficient electrosteric stability towards agglomeration in solution of the resultant nanocatalysts [2, 5, 6].



**Scheme 9.2** Schematic representation of steric stabilization.



**Scheme 9.3** *N*-alkyl-*N,N*-dimethyl-*N*-(2-hydroxyethyl)-ammonium chloride salt, a typical cationic surfactant which combines electrostatic and steric stabilizations (electrosteric stabilization).

The term “steric stabilization” may also be used to describe protective transition-metal colloids with traditional ligands or solvents. This stabilization occurs by: (i) the strong coordination of various metal nanoparticles with ligands such as phosphines [16–18], thiols [19–22], amines [21, 23–26], oxazolines [27] or carbon monoxide [18]; or (ii) weak interactions with solvents such as tetrahydrofuran (THF) or various alcohols [18, 28–31].

Finally, the development of modified nanoparticles having better stability and a longer lifetime has involved interesting results in diverse catalytic reactions. Efficient activities are obtained with these transition-metal colloids used as catalysts for the hydrogenation of various unsaturated substrates. Consequently, several recent investigations in total, partial or selective hydrogenation have received significant attention.

### 9.3

#### Hydrogenation of Compounds with C=C Bonds

Alkene hydrogenation is a common field of catalytic application for metal nanoparticles. Various approaches have been utilized to obtain stable and active nanocatalysts in hydrogenation reactions. The main approaches are described in the following sections, and are classified according to the stabilizing mode retained for the nanoparticles.

##### 9.3.1

#### Use of Polymers as Stabilizers

Organic polymers are very often used for the stabilization of metal nanoparticles by providing a steric stabilizing effect. Due to this embedding effect, it is generally considered that the diffusion of substrates through the polymer matrix can be limited. Nevertheless, some interesting results have been obtained.

Hirai and Toshima have published several reports on the synthesis of transition-metal nanoparticles by alcoholic reduction of metal salts in the presence of a polymer such as polyvinylalcohol (PVA) or polyvinylpyrrolidone (PVP). This simple and reproducible process can be applied for the preparation of monometallic [32, 33] or bimetallic [34–39] nanoparticles. In this series of articles, the nanoparticles are characterized by different techniques such as transmission electronic microscopy (TEM), UV-visible spectroscopy, electron diffraction (EDX), powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) or extended X-ray absorption fine structure (EXAFS, bimetallic systems). The great majority of the particles have a uniform size between 1 and 3 nm. These nanomaterials are efficient catalysts for olefin or diene hydrogenation under mild conditions (30 °C,  $P_{H_2}$  = 1 bar). In the case of bimetallic catalysts, the catalytic activity was seen to depend on their metal composition, and this may also have an influence on the selectivity of the partial hydrogenation of dienes.

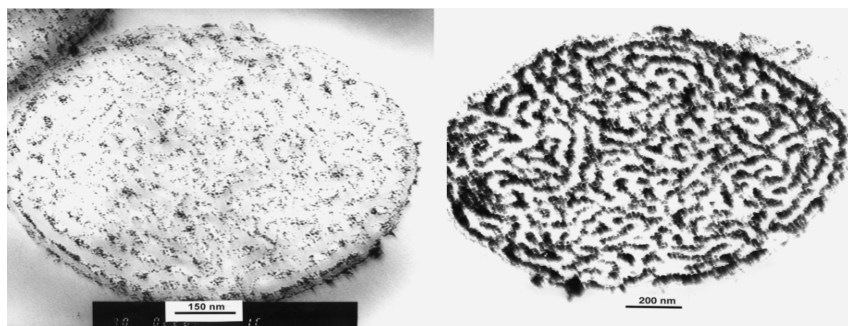
Delmas et al. produced PVP-stabilized rhodium nanoparticles using the method reported by Hirai [32] to perform catalytic hydrogenation of oct-1-ene in a two-liquid-phase system [40]. These authors investigated the effect of various parameters on nanoparticle stability and activity under more or less severe conditions. It was also shown that PVP/Rh colloids could be reused twice or more, without any loss of activity.

### 9.3.2

#### Use of Non-Usual Polymers as Stabilizers

Several groups have developed the use of non-usual polymers for the stabilization of colloids for hydrogenation catalysis. Mayer reported the use of various nonionic polymers and cationic polyelectrolytes as stabilizers for the synthesis of metal nanoparticles [41]; poly(1-vinylpyrrolidone-*co*-acrylic) and poly(2-ethyl-2-oxazoline) can be cited as examples here. Stable palladium and platinum colloids were prepared by the reduction of noble metal salts by refluxing the alcoholic solutions containing the polymers [42, 43]. Depending on the polymer used, a range of particle sizes and narrow size distributions were obtained. It appeared that a hydrophobic backbone and hydrophilic side chains are required for the nonionic polymers to become well stabilized and to provide controlled-size particles. Cationic polyelectrolytes also provided interesting results. With regard to catalysis, cyclohexene hydrogenation in MeOH was performed with Pd and Pt colloids, and conversions of 100% could be obtained in many cases. These authors also compared the activities of the nanocatalysts for this reaction depending on their protective polymer, polyelectrolyte or nonionic polymers [44]. In the same context, the ability of amphiphilic block copolymers, namely poly(dimethylsiloxane)-*b*-poly(ethylene oxide) (PDMS-*b*-PEO), polystyrene-*b*-poly(methacrylic acid) (PS-*b*-PMAA) and poly(styrene)-*b*-poly(ethylene oxide) (PS-*b*-PEO), to stabilize colloidal palladium, platinum, silver and gold nanoparticles has been investigated [45, 46]. Transmission electron microscopy (TEM) revealed randomly distributed nanoparticles with narrow size distributions in the range of 1 to 10 nm. In the case of Pd and Pt, cyclohexene hydrogenation has been chosen as model reaction for evaluation of the nanocatalysts. The influence of the precursor type, the polymer nature and also the preparation conditions on the catalytic activities have also been studied [46].

Liu et al. prepared palladium nanoparticles in water-dispersible poly(acrylic acid) (PAA)-lined channels of diblock copolymer microspheres [47]. The diblock microspheres (mean diameter 0.5  $\mu\text{m}$ ) were prepared using an oil-in-water emulsion process. The diblock used was poly(*t*-butylacrylate)-*block*-poly(2-cinnamoyloxyethyl) methacrylate (P*t*BA-*b*-PCEMA). Synthesis of the nanoparticles inside the PAA-lined channels of the microspheres was achieved using hydrazine for the reduction of PdCl<sub>2</sub>, and the nanoparticle formation was confirmed from TEM analysis and electron diffraction study (Fig. 9.1). The Pd-loaded microspheres catalyzed the hydrogenation of methylacrylate to methyl-propionate. The catalytic reactions were carried out in methanol as solvent under dihydro-



**Fig. 9.1** Transmission electron microscopy images of Pd-loaded PCEMA-*b*-PAA microspheres containing 27% Pd (left) and 63% Pd (right). (Adapted from [47])

gen bubbling. The catalysts were recovered by centrifugation and methanol washing, and recovery efficiency was 100%.

Bronstein et al. also used block copolymer micelles for the preparation of noble-metal monometallic or bimetallic colloids (Pd, Pd/Au) [48]. These colloids were characterized by electron microscopy and wide-angle X-ray scattering (WAXS) and studied in the hydrogenation of cyclohexene, 1,3-cyclooctadiene, and 1,3-cyclohexadiene. The catalytic reactions were carried out in toluene at 30 °C with [catalyst]/[substrate] molar ratios of 1:250 and 1:500 in the case of cyclohexene, and 1:500 and 1:10000 for 1,3-cyclohexadiene. High catalytic activities were obtained in the hydrogenation reactions, which were found to depend strongly on a number of parameters such as colloid morphology and reducing agent residues at the colloid surface. In fact, the strength of the reducing agent determines the rate of nucleation and growth of the colloids inside the micelle core and, consequently, a number of different architectures can be tailor-made. The second effect of the reducing agent used is provided by its residues or reaction products after reduction of the metal colloids that can influence the catalytic properties. Finally, Pd colloids could selectively hydrogenate 1,3-cyclohexadiene in cyclohexene with rates of between 10 to 1230 (Table 9.1). Nevertheless, it was observed that the hydrogenation of 1,3-cyclohexadiene is accompanied by the disproportionation of 1,3-cyclohexadiene to cyclohexene and benzene as a side reaction.

Akashi and coworkers prepared small platinum nanoparticles by ethanol reduction of  $\text{PtCl}_6^{2-}$  in the presence of various vinyl polymers with amide side chains [49]. These authors studied the effects of molecular weight and molar ratio [monomeric unit]/[Pt] on the particle sizes and size distributions by electron microscopy, and in some cases by the dispersion stability of the Pt colloids. The hydrogenation in aqueous phase of allyl alcohol was used as a model reaction to examine the change in catalytic activity of polymer-stabilized Pt colloids upon addition of  $\text{Na}_2\text{SO}_4$  to the reaction solution. The catalytic tests were performed in water or in  $\text{Na}_2\text{SO}_4$  aqueous solution at 25 °C under atmospheric pressure of

**Table 9.1** Activity of block copolymer-stabilized Pd colloids in selective hydrogenation of 1,3-cyclohexadiene. (Adapted from [48])

Catalyst <sup>a)</sup>	Reducing agent	Substrate/catalyst ratio [mol]	t [min]	substrate conversion [%]	Selectivity [%]			Rate <sup>c)</sup>
					Cyclohexene	Cyclohexane	Benzene	
PS-1,2; Na <sub>2</sub> PdCl <sub>4</sub>	super-hydride <sup>b)</sup>	500:1	10	100	71.3	0.1	28.6	40
PS-3,4; Pd(CH <sub>3</sub> COO) <sub>2</sub>	super-hydride	750:1	5	100	58.5	0.0	41.5	90
PS-3,4; Pd(CH <sub>3</sub> COO) <sub>2</sub>	NaBH <sub>4</sub>	10000:1	5	100	65.9	0.0	34.1	1230
PS-3,4; Pd(CH <sub>3</sub> COO) <sub>2</sub>	no reduction	500:1	25	100	60.1	5.4	34.5	10
Pd on activated carbon (Aldrich, 1 wt% Pd)	–	5000:1	7	100	54.7	0.7	44.6	420

- a) PS-1,2 and PS-3,4 are the two different chosen PS-*b*-P4VP block copolymers.  
 b) Superhydride = 1 M solution of LiB(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>H in THF.  
 c) Rate: mol cyclohexene min<sup>-1</sup> g<sup>-1</sup> atom metal as a total for both hydrogenation and disproportionation.

dihydrogen. 1-Propanol was the only product. The PNVF-Pt (PNVF = poly(*N*-vinylformamide)) colloid did not show any critical flocculation point, and was very stable in 0.8 M Na<sub>2</sub>SO<sub>4</sub> solution. Moreover, it provided the same activity as that obtained in pure water, while the other polymer-stabilized colloids showed markedly different behavior. The same authors described the synthesis of poly(*N*-isopropylacrylamide)-protected Au/Pt nanoparticles (mean diameter = 1.9 nm), their characterization by UV-visible spectroscopy, electron microscopy and X-ray diffraction, and their temperature-dependent catalytic activity in the aqueous hydrogenation of allyl alcohol [50]. The Au/Pt bimetallic colloids were found to have an alloy structure, the two metals being fully mixed, and were more active than the Pt monometallic colloids for the hydrogenation of allyl alcohol in water at room temperature. The hydrogenation rate was also seen to depend on the molar ratio of the Au/Pt in the bimetallic nanoparticles.

Recently, Liew et al. reported the use of chitosan-stabilized Pt and Pd colloidal particles as catalysts for olefin hydrogenation [51]. The nanocatalysts with a diameter ca. 2 nm were produced from PdCl<sub>2</sub> and K<sub>2</sub>PtCl<sub>4</sub> upon reduction with sodium borohydride in the presence of chitosan, a commercial biopolymer, under various molar ratios. These colloids were used for the hydrogenation of oct-1-ene and cyclooctene in methanol at atmospheric pressure and 30 °C. The catalytic activities in term of turnover frequency (TOF; mol. product mol. metal<sup>-1</sup> h<sup>-1</sup>)

**Table 9.2** Selective reduction of conjugated aromatic alkenes catalyzed by “Pd-PMHS” nanocomposites. (Reprinted with the permission of the American Chemical Society [52])

Substrate	Reaction conditions	Product	Yield [%]
Styrene	4 h/benzene/RT	Ethylbenzene	95 <sup>a)</sup>
4-Methoxystyrene	3 h/benzene/RT	1-Ethyl-4-methoxybenzene	95
2-Allylphenol	4 h/benzene/RT	2-Propylphenol	96
Cinnamitrile	5 h/benzene/RT	3-Phenylpropionitrile	90
2-Chlorostyrene	6 h/benzene/RT	(2-Chloroethyl)benzene	85
1,2-Diphenylethene	4 h/benzene/RT	1,2-Diphenylethane	94
2-Vinylnaphthalene	4 h/benzene/RT	2-Ethyl-naphthalene	96 <sup>b)</sup>
9-Vinylanthracene	6 h/benzene/RT	9-Ethylanthracene	92

a) All reactions performed with 2:1 molar equivalents of colloid:alkene and stirred under argon or nitrogen atmosphere. Reaction progress was monitored by <sup>1</sup>H-NMR and/or FT-IR spectroscopy.

b) Isolated yields.

RT = room temperature.

ranged from  $10^4 \text{ h}^{-1}$  to  $10^5 \text{ h}^{-1}$ . Chitosan-stabilized Pt and Pd colloids had similar catalytic properties for the hydrogenation of cyclooctene, which led to cyclooctane in both cases. By contrast, they showed different properties for the hydrogenation of oct-1-ene, in which Pd isomerized octene, giving rise to oct-2-ene and oct-3-ene. The activity of the nanocatalysts decreased with increasing concentration of chitosan.

The group of Chauhan has reported the preparation of polysiloxane-encapsulated Pd nanoclusters [52]. These colloids were synthesized by the reduction of Pd(OAc)<sub>2</sub> with polymethylhydrosiloxane, which functions as a reducing agent as well as a capping material. Chemoselective hydrogenation of functional conjugated alkenes was achieved by these polysiloxane-stabilized particles under mild conditions in high yields (Table 9.2). These authors also investigated the nature of the true catalyst by performing several experiments such as UV-visible studies of the precursor transformation in nanoclusters, TEM studies during catalysis, quantitative poisoning studies, and recyclability and reproducibility studies of the nanoclusters. All of the results obtained confirmed Pd-nanoclusters as the active catalytic species.

As a final example of catalytic hydrogenation activity with polymer-stabilized colloids, the studies of Cohen et al. should be mentioned [53]. Palladium nanoclusters were synthesized within microphase-separated diblock copolymer films. The organometallic repeat-units contained in the polymer were reduced by exposing the films to hydrogen at 100 °C, leading to the formation of nearly monodisperse Pd nanoclusters that were active in the gas phase hydrogenation of butadiene.



## 9.3.3

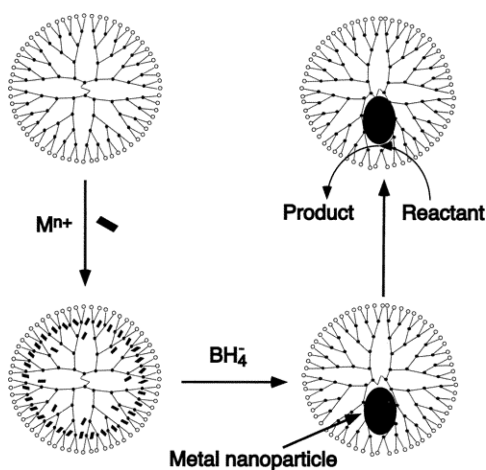
**Use of Dendrimers as Stabilizers**

The use of dendrimers constitutes an attractive stabilization mode for the synthesis of metal nanoparticles for several reasons:

- Due to their specific structure, which contains cavities with functional groups, they can act both as template and stabilizer for the nanoparticles.
- Dendrimers can also act as selective gates controlling the access of small molecules to the encapsulated nanoparticles.
- Tailoring of their terminal groups can enhance their solubility.

Dendrimer interior functional groups and cavities can retain guest molecules selectively, depending on the nature of the guest and the dendritic endoreceptors, the cavity size, the structure, and the chemical composition of the peripheric groups. Two main methods are known for the synthesis of metal nanoparticles inside dendrimers. The first method consists of the direct reduction of dendrimer-encapsulated metal ions (Scheme 9.4); the second method corresponds to the displacement of less-noble metal clusters with more noble elements [54].

The team of Crooks is involved in the synthesis and the use of dendrimers and, more particularly, poly(amidoamine) dendrimers (PAMAM), for the preparation of dendrimer-encapsulated mono- or bimetallic nanoparticles of various metals (Pt, Pd, Cu, Au, Ag, Ni, etc.) [55, 56]. The dendrimers were used as nanocatalysts for the hydrogenation of allyl alcohol and *N*-isopropylacrylamide or other alkenes under different reaction conditions (water, organic solvents, biphasic fluoruous/organic solvents or supercritical CO<sub>2</sub>). The hydrogenation reaction rate is dependent on dendrimer generation, as higher-generation dendrimers are more sterically



**Scheme 9.4** Schematic of metal nanoparticles synthesis within dendrimer templates. (Reprinted from [54]; copyright 2002, Marcel Dekker.)

**Table 9.3** Hydrogenation of alkenes using dendrimer-encapsulated Pd nanoparticles. <sup>a)</sup> (Reprinted with permission of the American Chemical Society [59])

Initial rate [mL H <sub>2</sub> min <sup>-1</sup> × 10]				
Substrate	Pd(0)/G <sub>3</sub> -TEBA	Pd(0)/G <sub>4</sub> -TEBA	Pd(0)/G <sub>5</sub> -TEBA	Pd/C
1,3-Cyclooctadiene	5.4	4.1	2.9	12.0
1,3-Cyclohexadiene	9.8	8.7	7.2	11.8
1,3-Cyclopentadiene	9.2	9.0	8.3	10.3
1-Heptene <sup>b)</sup>	0.98	0.90	0.88	0.0
Cyclohexene	0.92	0.80	0.70	2.8
Methylacrylate	9.5	9.0	7.6	10.0
<i>Tert</i> -Butylacrylate	5.5	4.5	3.1	9.1
Allyl alcohol	12.1	11.5	11.2	11.6
2-Methyl-3-buten-2-ol	5.8	4.2	3.8	9.3

- a) Reaction conditions: catalyst 5.0 μmol Pd, substrate 1.0 mmol, toluene 12.5 mL, H<sub>2</sub> 1 atm, 30 °C.  
 b) After 15 min, the reaction mixture contained *n*-hexane, 1-hexene, 2-hexene and 3-hexene.

crowded on their periphery and thus less porous and less likely to admit substrates to interior metal nanoparticles than those of lower generations. Another advantage of dendrimer-encapsulated nanoparticles is that they can be recycled.

Rhee and coworkers published the synthesis of bimetallic Pt-Pd nanoparticles [57] or Pd-Rh nanoparticles [58] within dendrimers as nanoreactors. These nanocatalysts showed a promising catalytic activity in the partial hydrogenation of 1,3-cyclooctadiene. The reaction was carried out in an ethanol/water mixture at 20 °C under dihydrogen at atmospheric pressure. The dendrimer-encapsulated nanoclusters could be reused, without significant loss of activity.

Kaneda et al. reported substrate-specific hydrogenation of olefins using the tri-ethoxybenzamide-terminated poly(propylene imine) dendrimers (PPI) as nanoreactors encapsulating Pd nanoparticles (mean diameter 2–3 nm) [59]. The catalytic tests were performed in toluene at 30 °C under dihydrogen at atmospheric pressure (Table 9.3). The hydrogenation rates were seen to decrease with increasing generation of dendrimers, from G<sub>3</sub> to G<sub>5</sub>.

#### 9.3.4

##### Use of Surfactants as Stabilizers

Surfactants are well known as stabilizers in the preparation of metal nanoparticles for catalysis in water. Micelles constitute interesting nanoreactors for the synthesis of controlled-size nanoparticles from metal salts due to the confinement of the particles inside the micelle cores. Aqueous colloidal solutions are then obtained which can be easily used as catalysts.

Toshima et al. obtained colloidal dispersions of platinum by hydrogen- and photo-reduction of chloroplatinic acid in an aqueous solution in the presence of various types of surfactants such as dodecyltrimethylammonium (DTAC) and sodium dodecylsulfate (SDS) [60]. The nanoparticles produced by hydrogen reduction are bigger and more widely distributed in size than those resulting from the photo-irradiation method. Hydrogenation of vinylacetate was chosen as a catalytic reaction to test the activity of these surfactant-stabilized colloids. The reaction was performed in water under atmospheric pressure of hydrogen at 30 °C. The photo-reduced colloidal platinum catalysts proved to be best in terms of activity, a fact explained by their higher surface area as a consequence of their smaller size.

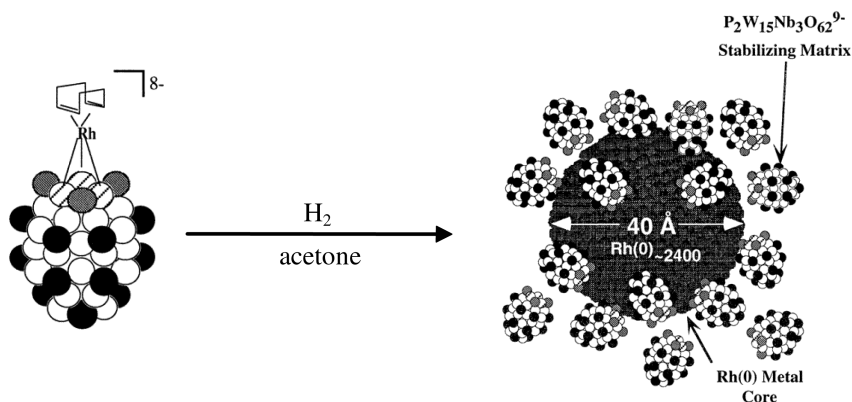
Larpernt and coworkers were interested in biphasic liquid–liquid hydrogenation catalysis [61], and studied catalytic systems based on aqueous suspensions of metallic rhodium particles stabilized by highly water-soluble trisulfonated molecules as protective agent. These colloidal rhodium suspensions catalyzed octene hydrogenation in liquid–liquid medium with TOF values up to 78 h<sup>-1</sup>. Moreover, it has been established that high activity and possible recycling of the catalyst could be achieved by control of the interfacial tension.

Gedanken et al. have reported the preparation of palladium nanoscale particles by sonochemical reduction of palladium acetate at room temperature in THF or methanol solution and in the presence of myristyltrimethylammonium bromide (CH<sub>3</sub>(CH<sub>2</sub>)<sub>13</sub>N(CH<sub>3</sub>)<sub>3</sub>Br) as stabilizing agent [62]. XRD and TEM with selected area electron diffraction (SAED) techniques confirmed that the stabilized-Pd nanoclusters were nanocrystalline and composed of aggregates of spherical particles of size 10–20 nm. Cyclohexene hydrogenation reactions were carried out in diethyl ether under a hydrogen atmosphere (ca. 0.2 MPa) at room temperature. The formation of cyclohexane could be observed with a conversion of 64%, which was higher than that obtained using a commercial Pd/C catalyst.

### 9.3.5

#### Use of Polyoxoanions as Stabilizers

An original method for the stabilization of metal nanoparticles destined for catalytic applications was developed by Finke et al., who produced polyoxoanion- and tetrabutylammonium-stabilized iridium and rhodium nanoparticles (Scheme 9.5) [63, 64]. The synthesis method consists of the hydrogen reduction, in acetone, of the polyoxoanion-supported Ir(I) or Rh(I) complex [(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>5</sub>-Na<sub>3</sub>[(1,5-COD)Rh·P<sub>2</sub>W<sub>15</sub>Nb<sub>3</sub>O<sub>62</sub>]. The resultant Rh(0) nanoclusters are near-monodisperse with a mean size of 4±0.6 nm, and can be isolated as a black powder and redispersed in non-aqueous solvents such as acetonitrile. The particles have been characterized by a variety of techniques, including TEM, energy-dispersive spectroscopy, electron diffraction, UV-visible spectroscopy and elemental analysis. Ion-exchange chromatography revealed that the Rh(0) nanoclusters are stabilized by the adsorption of the polyoxoanion onto their outer surface. These nanoclusters were active in cyclohexene hydrogenation at room



**Scheme 9.5** Synthesis of Rh(0) nanoclusters from (1,5-COD)RhP<sub>2</sub>W<sub>15</sub>Nb<sub>3</sub>O<sub>62</sub><sup>9-</sup> polyoxoanion-supported nanocluster-forming precatalyst (space-filling representation). (Adapted from [63].)

temperature and under dihydrogen pressure, with TOF of 3650 h<sup>-1</sup>. In another report, the same group studied the in-solution lifetimes of Rh(0) nanocatalysts; these were found to approach those of a solid-oxide-supported Rh(0) catalyst, with values higher than were previously reported [65].

### 9.3.6

#### Use of Ligands as Stabilizers

The use of ligands as protective agents for metal nanoparticle synthesis has become increasingly common during the past few years. The main advantage of this stabilizing mode for nanocatalysts is the possibility of modulating the surface state of the particles by chemical influence of the ligand. Nevertheless, it is necessary to identify ligands that give rise to stable, but active, nanocatalysts. Until now, the ligands used have been generally simple organic ligands (thiols, amines, carboxylic acids, phosphines), though on occasion more sophisticated ligands are used such as phenanthroline,  $\beta$ -cyclodextrins or ferritines.

As an initial example, Sastry et al. [66] described a single-step procedure for the synthesis of catalytically active, hydrophobic platinum nanoparticles involved in the spontaneous reduction of aqueous PtCl<sub>6</sub><sup>2-</sup> ions by hexadecylaniline (HDA) at a liquid–liquid interface. HDA acts simultaneously as phase-transfer molecule, reducing agent and nanoparticle capping agent. The HDA chloroform solution of nanoparticles could be isolated as a black powder after solvent evaporation, while any uncoordinated HDA was removed by ethanol washing. The nanoparticles could then be redispersed in organic solvents (benzene, toluene, hexane). UV-visible, TEM and XRD measurements confirmed the formation of Pt nanoparticles of mean size 15.5±0.7 nm and with a face-centered cubic structure, while TGA analysis showed desorption of the HDA molecule (a weight

loss of 30% at 270 °C) and  $^1\text{H-NMR}$  spectra proved close contact of the ligand with the metal surface. These Pt nanoparticles were investigated in styrene hydrogenation under  $\text{H}_2$  pressure (14 bar) at 60 °C, and showed complete conversion into ethylbenzene with a TOF of  $655\text{ h}^{-1}$ . They were also active in cyclohexene hydrogenation, allowing complete conversion into cyclohexane with 100% selectivity and a TOF of  $2112\text{ h}^{-1}$ .

Vargaftik and Moiseev have obtained near-spherical palladium nanoclusters with an average size of 1.8 nm by reduction of palladium carboxylates  $\text{Pd}_3(\text{OCOR})_6$  ( $\text{R}=\text{Me, Et, CHMe}_2, \text{CMe}_3$ ) with hydrogen in alcohol solutions containing 1,10-phenanthroline as ligand [67]. Based on elemental analysis, NMR, X-ray photoelectron spectroscopy and EXAFS investigations, these nanoclusters were described by the idealized formula  $\text{Pd}_{147}\text{phen}_{32}\text{O}_{60}(\text{OCOR})_{30}$ . These nanocatalysts were used in the hydrogenation of alkynes and alkenes, the reduction of nitriles with formic acid, and the oxidation of aliphatic and benzylic alcohols. For alkene hydrogenation, styrene was used as substrate, the catalytic reaction being performed in alcohol at temperatures up to 70 °C. The results revealed that Pd-147 nanoclusters were much more active than the giant Pd-561 clusters or the traditional Pd/C catalyst. By comparison, ethylbenzene has been produced using all three catalysts, with respective TOF values of 242, 155, and  $25\text{ h}^{-1}$ , respectively, at 20 °C.

Sahle-Demessie and Pillai studied the catalytic activity of phenanthroline-stabilized palladium nanoparticles in polyethylene glycol (PEG) as a recyclable catalyst system for the selective hydrogenation of olefins using molecular hydrogen under mild reaction conditions [68]. PEG acts not only as a reducing agent but also as a dispersing medium for the ligand-stabilized nanoparticles. The phenanthroline-stabilized Pd nanoparticles are well defined, with a mean size of 2–6 nm. Hydrogenation of various olefins (cyclohexene, then aliphatic, alicyclic and aromatic olefins) was performed in liquid phase under hydrogen at atmospheric pressure; some results are presented in Table 9.4. The catalyst system was found to be active and selective for the hydrogenation of a variety of olefins, with good to excellent conversion. In the case of 1,5-cyclooctadiene, cyclooctene is formed, but the selectivity of the di-hydrogenated product was enhanced with an increase in reaction time. The hydrogenation of unsaturated alcohols, aldehydes and ketones, such as cinnamyl alcohol and citral, formed the C=C hydrogenated product selectively without affecting the C=O group. However, the selectivity of the di-hydrogenated product also increased with reaction time. The catalyst system was easily separable from the reaction mixture by extraction of the products with diethyl ether, and could be reused several times (six cycles) without any loss of activity or selectivity. These authors demonstrated that phenanthroline stabilizes the palladium nanoparticles in PEG, which may act as a mobile supporting phase, thereby achieving high stability and high activity for the catalyst system.

Kaifer and coworkers showed interest in the modification of metal nanoparticles with organic monolayers prepared with suitable molecular hosts. They reported the preparation of water-soluble platinum and palladium nanoparticles modified with thiolated  $\beta$ -cyclodextrin ( $\beta$ -CD) [69]. Nanoparticle synthesis was

**Table 9.4** Phenanthroline-stabilized palladium nanoparticles in PEG for the hydrogenation of alkenes.<sup>a)</sup> (Adapted from [68])

Substrate	Product	Temp. [°C]	Time [h]	Conversion [%]	Selectivity [%]	TON
Cyclopentene	Cyclopentane	30	20	100	100	448
1-Hexene	<i>n</i> -Hexane	50	8	100	100	448
Cyclohexene	Cyclohexane	30	8	100	100	448
1-Methyl Cyclohexene	Methyl cyclohexane	50	20	54	100	242
1-Phenyl Cyclohexene	Phenyl cyclohexane	50	20	100	94 <sup>b)</sup>	448
1-Octene	<i>n</i> -Octane	50	8	100	100	448
2-Octene	<i>n</i> -Octane	50	20	100	100	448
Cyclooctene	Cyclooctane	50	8	100	100	448
1,5-Cyclooctadiene	Cyclooctene	40	20	100	38 <sup>c)</sup>	448
Styrene	Ethyl benzene	30	20	100	100	448
Stilbene	Dibenzyl	50	4	100	100	448
Norbornylene	Norborane	40	4	100	100	448
Cinnamyl alcohol	3-Phenyl propanol	40	20	100	100	448
Citral	Citronellal	50	20	100	15 <sup>d)</sup>	448
3-Methyl-2-butenal	3-Methyl butyraldehyde	40	8	94	100	422
Mesityl oxide	4-Methyl-2- pentanone	40	8	94	100	422
Cyclohexenone	Cyclohexanone	40	8	51	100	229
3-Methyl cyclohexene-1-ol	3-Methyl cyclohexanol	40	20	100	100	448

a) Reaction conditions: 10 mmol substrate, 5 mg Pd acetate, 1.5–3.0 mg 1,10-phenanthroline, 4 g PEG (400), stir, H<sub>2</sub> balloon.

b) Remaining biphenyl.

c) Remaining cyclooctane.

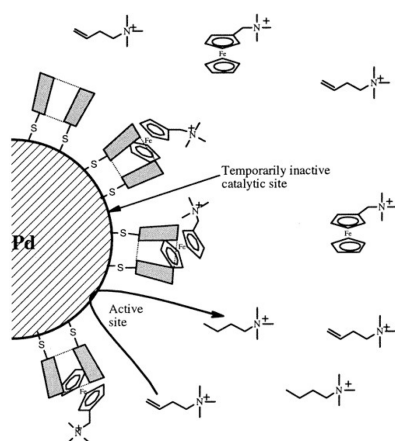
d) Remaining hydrocitronellal.

TON: calculated as the number of moles product formed per mol palladium.

realized by the reduction of a DMSO-water solution of Na<sub>2</sub>PtCl<sub>4</sub> (or Na<sub>2</sub>PdCl<sub>4</sub>) by NaBH<sub>4</sub> in the presence of HS-β-cyclodextrin at room temperature. The nanoparticles were isolated as a dark precipitate after the addition of ethanol. Centrifugation and washing with DMSO and ethanol, followed by drying at 60 °C, provided dried powders containing Pt or Pd nanoparticles with a respective mean size of 14.1±2.2 and 15.6±1.3 nm. These Pt and Pd nanoparticles could be redispersed in water, and were tested for catalytic allylamine hydrogenation under atmospheric pressure of H<sub>2</sub> and room temperature (Table 9.5). Both types of CD-modified metal nanoparticles were soluble in the reaction media and could be easily recovered at the end of the reaction by precipitation with ethanol.

**Table 9.5** Percentage conversion from allylamine (1.8 mmol) to propylamine obtained with cyclodextrin (CD)-modified Pt and Pd nanoparticles under 1.0 atm  $H_2(g)$  at room temperature in  $D_2O$  solution (2.0 mL). (Reprinted with permission of the Royal Society of Chemistry [69])

Catalyst	Quantity [mg]	Time [h]	Conversion [%]
CD-mod. Pt	10	6	>95
CD-mod. Pd	10	6	100
None	—	6	0
CD-mod. Pt	5	1	10
CD-mod. Pd	5	1	30



**Scheme 9.6** Deactivation of active catalytic sites by binding ferrocene derivatives to the CD hosts on the Pd nanoparticles. (Reprinted with permission of the American Chemical Society [70].)

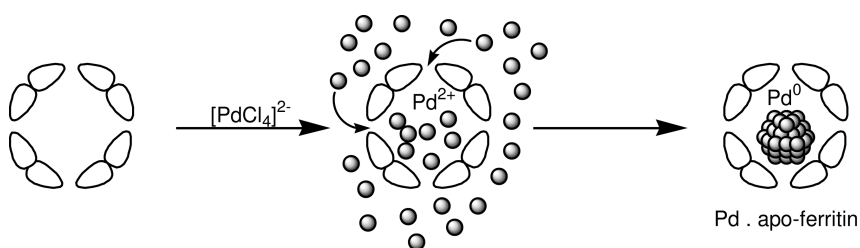
Following the same procedure, these authors also reported [70] water-soluble Pd nanoparticles (diameter  $3.5 \pm 1.0$  nm) which were modified with covalently attached cyclodextrin receptors and obtained by  $NaBH_4$  reduction of  $PdCl_4^{2-}$  in dimethylformamide solution containing perthiolated  $\beta$ -CD. After characterization by usual methods (TEM, UV-visible, NMR), hydrogenation of 1-butenyl(trimethyl)ammonium bromide under  $H_2$  (1 atm) in  $D_2O$  at  $25^\circ C$  gave a TOF of  $320 h^{-1}$ . Since these Pd nanoparticles behave as active catalyst for the hydrogenation of alkenes in aqueous media, the group investigated whether this catalytic activity could be modulated through binding of guests to the surface-immobilized CD hosts. Since it is well known that ferrocene derivatives form stable inclusion complexes with  $\beta$ -CD, ferrocene compounds were added to the reaction mixture (Scheme 9.6). Under these circumstances, a substantial reduction in the rate of hydrogenation, dependent upon the ferrocene concentration, was noted. In addition, the catalytic ability of such a system for the hydrogenation of an olefin bearing a ferrocenyl group was compared. The inhibitory effect was lower in this case, probably because of the affinity of the olefin through its ferrocene moiety for the

CD-modified nanoparticles sites. These studies afford an interesting example of “tunable catalyst” design at the molecular level. Manipulation of the surface of catalytically active metal nanoparticles seems possible, and can be used to modulate the catalytic activity on demand.

### 9.3.7

#### Biomaterial as a Protective Matrix

Ueno et al. have published results relating to olefin hydrogenation by a Pd nanocluster confined in an apo-ferritin cage [71]. Ferritin, an iron-storage protein, comprises 24 subunits that assemble to form a hollow cage-like structure with a diameter of 12 nm and an internal cavity of 8 nm. These authors used ferritin as a stabilizing agent for the synthesis of Pd nanoparticles and their use in hydrogenation catalysis. The aqueous synthesis was realized by reduction of  $K_2PdCl_4$  with  $NaBH_4$  in the presence of apo-ferritin, giving rise to a clear brown solution containing monodispersed spherical Pd nanoparticles with a mean size of



**Scheme 9.7** Schematic synthesis of apo-ferritin stabilized-Pd nanoparticles. (Reprinted with permission of Wiley [71].)

**Table 9.6** Hydrogenation activity of Pd-apo-ferritin nanoparticles in water. (Reprinted with permission of Wiley [71].)

Olefin	TOF [ $h^{-1}$ ] for Pd apo-ferritin <sup>a), b)</sup>	TOF [ $h^{-1}$ ] for Pd particles <sup>b), c)</sup>
$CH_2=CHCONH_2$ (1)	$72 \pm 0.7$	$58 \pm 5.9$
$CH_2=CHCOOH$ (2)	$6.3 \pm 1.1$	$12 \pm 2.6$
$CH_2=CHCONH-iPr$ (3)	$51 \pm 6.5$	$15 \pm 0.3$
$CH_2=CHCONH-tBu$ (4)	$31 \pm 5.9$	$6.1 \pm 0.6$
$CH_2=CHCO-Gly-OMe$ (5)	$6.3 \pm 3.8$	$28 \pm 2.6$
$CH_2=CHCO-D,L-Ala-OMe$ (6)	Not detected	$23 \pm 0.3$

- a) Hydrogenation reactions catalyzed by Pd apo-ferritin carried out at 7 °C (pH 7.5) with 30  $\mu$ M Pd.  
 b) TOF = [product(mol)] per atom Pd per hour.  
 c) The same conditions were used, but apo-ferritin was omitted.



2.0±0.3 nm (Scheme 9.7). The catalytic hydrogenation of olefins (acrylamide derivatives) by Pd apo-ferritin nanoparticles was evaluated in aqueous medium (Table 9.6). Since the observed TOFs are dependent upon substrate size, it could be concluded that Pd-apo-ferritin particles induce size-selective olefin hydrogenation.

### 9.3.8

#### Ionic Liquids used as Templates for the Stabilization of Metal Nanoparticles

More efficient catalytic systems that might combine the advantages of both homogeneous (catalyst modulation) and heterogeneous catalysis (catalyst recycling) are the subjects of great attention by the scientific community working on catalysis. For such purpose, ionic liquids are interesting systems as they can provide simple product separation and catalyst recycling.

The group of Dupont has developed the synthesis of metal nanoparticles in ionic liquids for use as catalysts. The group has published several reports relating to ionic liquid-stabilized nanoparticles of various metals, including iridium [72], platinum [73] and ruthenium [74]. Mostly, the nanoparticles are synthesized from organometallic precursors such as [Ir COD Cl]<sub>2</sub>, Pt<sub>2</sub>(dba)<sub>3</sub> or Ru COD COT (COD=cycloocta-1,5-diene; COT=cycloocta-1,3,5-triene; dba=dibenzylideneacetone). The decomposition of these complexes is accomplished under molecular hydrogen (4 atm) at 75 °C in the chosen ionic liquid such as 1-*n*-butyl-3-methylimidazolium hexafluorophosphate (BMI PF<sub>6</sub>) or 1-*n*-butyl-3-methylimidazolium tetrafluoroborate (BMI BF<sub>4</sub>). These reaction conditions lead to well-dispersed nano-

**Table 9.7** Catalytic performance of Pt(0) nanoparticles in solventless, homogeneous, and biphasic conditions.<sup>a)</sup>  
(Reprinted with permission of the American Chemical Society [73].)

Medium	Substrate	Product	Time [h]	Conversion [%] <sup>b)</sup>	TOF [h <sup>-1</sup> ] <sup>c)</sup>
Solventless	Hex-1-ene	Hexane	0.25	100	1000
Acetone	Hex-1-ene	Hexane	0.25	100	1000
BMI PF <sub>6</sub>	Hex-1-ene	Hexane	0.4	100	625
BMI PF <sub>6</sub>	Cyclohexene	Cyclohexane	1.6	100	156
Solventless	Cyclohexene	Cyclohexane	0.3	100	833
Acetone	Cyclohexene	Cyclohexane	0.3	100	833
BMI PF <sub>6</sub>	2,3-Dimethyl-1-butene	2,3-Dimethylbutane	3	82	68
Solventless	2,3-Dimethyl-1-butene	2,3-Dimethylbutane	0.6	100	417
Solventless	1,3-Cyclohexadiene	Cyclohexane	0.3	100	833

a) Reaction conditions: [substrate]/[Pt]=250 at 75 °C and under 4 atm H<sub>2</sub> (constant pressure).

b) Substrate conversion.

c) [mol product] [mol Pt]<sup>-1</sup> [h].

**Table 9.8** Hydrogenation of alkenes by Ru(0) nanoparticles under multiphase and solventless conditions (75 °C and constant pressure of 4 atm, substrate/Ru=500). (Adapted from [74])

Medium	Substrate	Time [h]	Conversion [%]	TON <sup>a)</sup>	TOF [h <sup>-1</sup> ] <sup>b)</sup>
Solventless	1-hexene	0.7	>99	500	714
BMI BF <sub>4</sub>	1-hexene	0.6	>99	500	833
BMI PF <sub>6</sub>	1-hexene	0.5	>99	500	1000
Solventless	cyclohexene	0.5	>99	500	1000
BMI BF <sub>4</sub>	cyclohexene	5.0	>99	500	100
BMI PF <sub>6</sub>	cyclohexene	8.0	>99	500	62
Solventless	2,3-dimethyl-2-butene	1.2	76	380	316

a) Turnover number (TON) = mol hydrogenated product mol<sup>-1</sup> Ru.

b) Turnover frequency (TOF) = TON h<sup>-1</sup>.

metric particles ( $d_m = 2\text{--}3$  nm) in the ionic liquid. The thus-obtained nanoparticles are stable and isolable by centrifugation and acetone washing, and were characterized using a variety of techniques such as TEM, XRD, EDX, or XPS. The isolated nanoparticles can be redispersed in the ionic liquid, acetone, or used in solventless conditions for respectively, liquid–liquid biphasic, homogeneous or heterogeneous hydrogenation of alkenes and arenes under mild conditions (75 °C, 4 atm). Various olefins were used as substrates for the catalytic experiments, and results obtained with the Pt and Ru nanoparticles are listed in Tables 9.7 and 9.8, respectively. In general, the best results were obtained in solventless conditions. The recovered catalysts could be reused as solids or redispersed in the ionic liquid several times, without significant loss in catalytic activity.

In order to avoid the problem of aggregation, some research groups have studied the addition of a stabilizer (ligand or polymer) to increase stability of the nanocatalysts in ionic liquid. Han and coworkers reported the use of ligand-stabilized palladium nanoparticles for the hydrogenation of olefins in an ionic liquid [75]. These authors prepared phenanthroline-stabilized Pd nanoparticles (2–5 nm) in BMIM PF<sub>6</sub> and tested them directly as catalyst for olefin hydrogenation at 40 °C. The catalytic system showed high activity, with TOFs up to 234 h<sup>-1</sup>, and the catalyst could be recycled (Table 9.9). The authors proposed that the ligand protected the Pd nanoparticles while the ionic liquid acted as a mobile support for the nanocatalyst and enhanced their stability.

Similarly, Kou et al. published the synthesis of PVP-stabilized noble-metal nanoparticles in ionic liquids BMI PF<sub>6</sub> at room temperature [76]. The metal nanoparticles (Pt, Pd, Rh) were produced by reduction of the corresponding metal halide salts in the presence of PVP into a refluxing ethanol-water solution. After evaporation to dryness the residue was redissolved in methanol and the solution added to the ionic liquid. The methanol was then removed by evaporation to give the ionic liquid-immobilized nanoparticles. These nanoparticles were very stable. TEM ob-

**Table 9.9** Hydrogenation of olefins catalyzed by Phen-protected Pd nanoparticles in [BMIM][PF<sub>6</sub>].<sup>a)</sup>  
(Adapted from [75])

Olefin	Olefin/Pd [mol mol <sup>-1</sup> ]	Temperature [°C]	Time [h]	Conversion [%]
Cyclohexene	2000	40	2.0	35
Cyclohexene	500	40	5.0	100
Cyclohexene	500	30	7.0	100
Cyclohexene	500	50	4.0	100
Cyclohexene	500	60	3.5	100
1-Hexene	500	20	3.0	100
1-Hexene	500	40	1.5	100
1,3-Cyclohexadiene	500	40	2.0	95 <sup>b)</sup>
1,3-Cyclohexadiene	500	40	7.0	100 <sup>c)</sup>

a) 1 bar H<sub>2</sub> (constant pressure).

b) Product is cyclohexene; no cyclohexane was detected.

c) Product is cyclohexane.

servations indicated that the distribution of particles size in the range 2–5 nm were similar before and after their immobilization in the ionic liquid. The catalytic performance was evaluated in the hydrogenation of olefins at 40 °C under hydrogen pressure (1 atm) in biphasic conditions (Table 9.10). The results showed that nanoparticles were highly active catalysts for the hydrogenation of olefins under very mild conditions. The ionic liquid-immobilized nanoparticles were easily separated from the product mixture by simple decantation or reduced pressure distillation, and could be reused several times, without loss of activity. TEM analysis carried out after several catalytic experiments showed that the particles did not aggregate; thus, the combination of PVP and ionic liquid appeared to be successful in inhibiting particle aggregation.

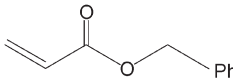
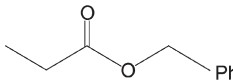
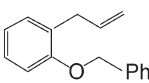
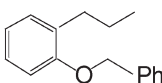
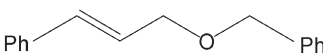
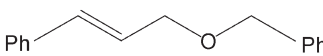

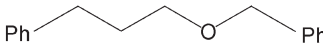
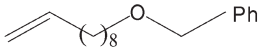
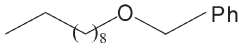
**Table 9.10** Hydrogenation of alkenes catalyzed by PVP-stabilized noble-metal nanoparticles in [BMIM][PF<sub>6</sub>].  
(Adapted from [76])

Substrate	Metal	Substrate/metal [mol mol <sup>-1</sup> ]	Time [h]	Conversion [%] <sup>a)</sup>	TOF [h <sup>-1</sup> ] <sup>b)</sup>
Cyclohexene	Pt	2000	16	100	125
1-Hexene	Pt	1000	1	100	1000
1-Dodecene	Pt	1000	1	100	1000
Cyclohexene	Pd	250	1	100	250
Cyclohexene	Rh	250	2	100	125

a) Substrate conversion.

b) Turnover frequency (TOF) = [mol product] [mol metal]<sup>-1</sup> h<sup>-1</sup>.

**Table 9.11** Hydrogenation reactions with Pd nanocatalysts in methanol, toluene or [BMIM][PF<sub>6</sub>].<sup>a)</sup> (Adapted from [77])

Substrate	Time [h]	Product	Yield [%]
	20		97
	22		98
	20		82
			17
	40		92

a) Reactions carried out at room temperature using a balloon filled with H<sub>2</sub> and 0.001 equiv. Pd<sub>0</sub>Ac as catalyst in [BMIM][PF<sub>6</sub>] as solvent. Substrate/metal ratio=100.

Recently, tetrabutylammonium bromide-stabilized Pd nanoparticles have been described for the hydrogenation of carbon-carbon double bonds bearing benzyloxy groups in [BMIM][PF<sub>6</sub>] under 1 bar of hydrogen and at room temperature [77]. Some results are summarized in Table 9.11. The nanoparticles were synthesized from PdCl<sub>2</sub> or Pd(OAc)<sub>2</sub> precursors. These metal salts were mixed with tetrabutylammonium bromide and heated under vacuum at 120 °C before addition of tri-*n*-butylamine (*n*-Bu<sub>3</sub>N) and an additional treatment at 120 °C for 3 h. The black powders formed could be isolated and characterized by a variety of techniques (IR, NMR, elemental analysis, TEM). TEM analysis revealed dispersed nanoparticles ( $d_m=4.1\pm 1.0$  nm) in the case of Pd(OAc)<sub>2</sub> as precursor, but agglomerated particles ( $d_m=7.5\pm 1.7$  nm) with PdCl<sub>2</sub>. It appeared that the hydrogenation of double bonds was chemoselective. Recycling of the system [BMIM][PF<sub>6</sub>]/palladium nanoparticles has been carried out, without noticeable modification of the chemoselectivity and yield.

### 9.3.9

#### Supercritical Microemulsions Used as Templates for the Stabilization of Metal Nanoparticles



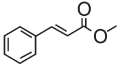
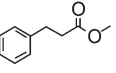
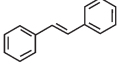
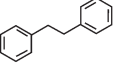
In recent years, supercritical fluids such as scCO<sub>2</sub> were considered to be modern “green” solvents: they were non-toxic, readily available, inexpensive, and environmentally benign. They are studied as a reaction medium for catalytic applications because of their interest in product separation and catalyst recovery, and

several reports have described the use of metal nanoparticles in supercritical fluids.

Wai et al. used water-in-CO<sub>2</sub> microemulsions as a medium for synthesizing metallic Pd nanoparticles [78]. The water-in-CO<sub>2</sub> microemulsion was prepared by mixing an aqueous PdCl<sub>2</sub> solution with a mixture of bis(2-ethylhexyl)sulfosuccinate (AOT) as surfactant and perfluoropolyetherphosphate (PFPE-PO<sub>4</sub>) as co-surfactant into CO<sub>2</sub> at 80 atm to ensure the formation of an optically transparent microemulsion. Injection of dihydrogen into the microemulsion allowed the formation of Pd nanoparticles in the size range 5–10 nm, as confirmed by UV-visible spectroscopy and TEM analysis. The hydrogenation of 4-methoxy-cinnamic acid to 4-methoxyhydrocinnamic acid was performed first in liquid CO<sub>2</sub> and then in supercritical CO<sub>2</sub> at 35 °C and 50 °C. The hydrogenation process is much faster in the scCO<sub>2</sub> phase (35 and 50 °C) compared with that in the liquid CO<sub>2</sub> phase (20 °C), probably due to a better diffusion of the reactant from bulk CO<sub>2</sub> to the Pd nanoparticles surface, the diffusion coefficient of CO<sub>2</sub> dramatically changing at the critical point (31 °C). *Trans*-stilbene and maleic acid hydrogenations were also performed, undergoing the production of 1,2-diphenyl-ethane and succinic acid respectively, as determined by NMR investigation.

The same authors also reported the dispersion of palladium nanoparticles in a water/AOT/*n*-hexane microemulsion by hydrogen gas reduction of PdCl<sub>4</sub><sup>2-</sup> and its efficiency for hydrogenation of alkenes in organic solvents [79]. UV-visible spectroscopy and TEM analysis revealed the formation of Pd nanoparticles with diameters in the range of 4 to 10 nm. Three olefins (1-phenyl-1-cyclohexene, methyl *trans*-cinnamate, and *trans*-stilbene) were used as substrates for the catalytic hydrogenation experiments under 1 atm of H<sub>2</sub> (Table 9.12). All of the start-

**Table 9.12** Catalytic hydrogenation of olefins with Pd nanoparticles in a water-in-hexane microemulsion. (Reprinted with the permission of the American Chemical Society [79])

Olefin	Catalyst	Reaction time [min]	Conversion [%]	Product
	Pd/ME <sup>a)</sup>	5	>97	
	Pd/C <sup>b)</sup>	20	50	
	Pd/C <sup>b)</sup>	40	>97	
	Pd/ME <sup>a)</sup>	6	>97	
	Pd/C <sup>b)</sup>	25	60	
	Pd/C <sup>b)</sup>	45	>97	
	Pd/ME <sup>a)</sup>	7	>97	
	Pd/C <sup>b)</sup>	40	68	
	Pd/C <sup>b)</sup>	60	>97	

a) Molar ratio of alkene/AOT/Na<sub>2</sub>PdCl<sub>4</sub> = 1/1/0.01 and 10 mL of *n*-hexane used as solvent (W = 15) at 30 °C.

b) 1.7 mg Pd/C (0.17 mg or 1.6 μmol Pd) in 10 mL *n*-hexane.

ing alkenes were converted into the saturated hydrocarbons within 6–7 min, while the Pd nanoparticles dispersed in the microemulsion proved to be more efficient catalysts than the Pd/C catalyst tested for comparison.

### 9.3.10

#### Conclusion

A variety of approaches has been explored for the synthesis of metal nanoparticles, with the objective of using them as catalysts for alkenes hydrogenation. It appears, clearly, that whichever the chosen stabilizing mode, it is possible to obtain active nanoparticles for olefin hydrogenation. Nevertheless, the activities obtained are difficult to compare as the experimental conditions are, by necessity, different. Even if the tested catalytic reaction is for most of the time the hydrogenation of simple olefins, other colloidal systems have permitted the hydrogenation of more interesting alkenes. Recycling of the nanocatalysts is also of major interest, as colloidal catalysts may be considered to be pseudo-homogeneous catalysts (soluble nanocatalysts) with clear advantages over their heterogeneous counterparts. Indeed, colloidal nanoparticles represent highly interesting systems for the future development of catalysis in terms of both activity and selectivity.

## 9.4

### Hydrogenation of Compounds with $C\equiv C$ Bonds

The use of dispersed or immobilized transition metals as catalysts for partial hydrogenation reactions of alkynes has been widely studied. Traditionally, alkyne hydrogenations for the preparation of fine chemicals and biologically active compounds were only performed with heterogeneous catalysts [80–82]. Palladium is the most selective metal catalyst for the semihydrogenation of mono-substituted acetylenes and for the transformation of alkynes to *cis*-alkenes. Commonly, such selectivity is due to stronger chemisorption of the triple bond on the active center.

The liquid-phase hydrogenation of various terminal and internal alkynes under mild conditions was largely described with metal nanoparticles deposited/incorporated in inorganic materials [83, 84], although several examples of selective reduction achieved by stabilized palladium, platinum or rhodium colloids have been reported in the literature.

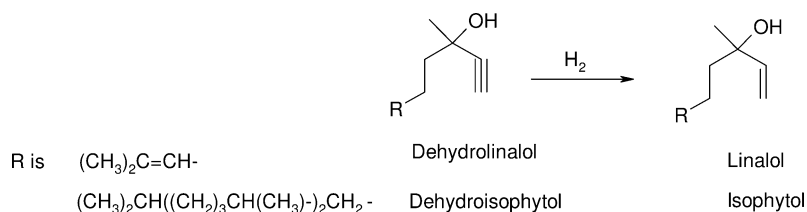
The selective hydrogenation of hex-2-yne into *cis*-hex-2-ene with Pd colloids stabilized by 1,10-phenanthroline and derivatives has been reported by Schmid. Selectivity in alkenes up to 99% was obtained [25]. The use of PVP-stabilized Pt colloids with an average particle size of 1.4 nm dispersed in a propanol mixture prepared from  $Pt_2(dba)_3$  provided 81% and 62% selectivity to *cis*-hexene at 50% and 90% hex-2-yne conversion, respectively. Bradley has shown that selectivity up to 89% in *cis*-hex-2-ene could be obtained with colloids supported in an

amorphous microporous mixed oxides [85]. Following the adapted procedure, Bönnemann performed the hydrogenation of hex-3-yn-1-ol into *cis*-hex-3-en-1-ol with previously synthesized Pd colloids and immobilized on CaCO<sub>3</sub>; the obtained selectivity was about 98% [86].

Partial hydrogenation of acetylenic compounds bearing a functional group such as a double bond has also been studied in relation to the preparation of important vitamins and fragrances. For example, selective hydrogenation of the triple bond of acetylenic alcohols and the double bond of olefin alcohols (linalol, isophytol) was performed with Pd colloids, as well as with bimetallic nanoparticles Pd/Au, Pd/Pt or Pd/Zn stabilized by a block copolymer (polystyrene-poly-4-vinylpyridine) (Scheme 9.8). The best activity (TOF 49.2 s<sup>-1</sup>) and selectivity (>99.5%) were obtained in toluene with Pd/Pt bimetallic catalyst due to the influence of the modifying metal [87, 88].

Recently, Chaudhari compared the activity of dispersed nanosized metal particles prepared by chemical or radiolytic reduction and stabilized by various polymers (PVP, PVA or poly(methylvinyl ether)) with the one of conventional supported metal catalysts in the partial hydrogenation of 2-butyne-1,4-diol. Several transition metals (e.g., Pd, Pt, Rh, Ru, Ni) were prepared according to conventional methods and subsequently investigated [89]. In general, the catalysts prepared by chemical reduction methods were more active than those prepared by radiolysis, and in all cases aqueous colloids showed a higher catalytic activity (up to 40-fold) in comparison with corresponding conventional catalysts. The best results were obtained with cubic Pd nanosized particles obtained by chemical reduction (Table 9.13).

Catalytic studies and kinetic investigations of rhodium nanoparticles embedded in PVP in the hydrogenation of phenylacetylene were performed by Choukroun and Chaudret [90]. Nanoparticles of rhodium were used as heterogeneous catalysts (solventless conditions) at 60 °C under a hydrogen pressure of 7 bar with a [catalyst]/[substrate] ratio of 3800. Total hydrogenation to ethylbenzene was observed after 6 h of reaction, giving rise to a TOF of 630 h<sup>-1</sup>. The kinetics of the hydrogenation was found to be zero-order with respect to the alkyne compound, while the reduction of styrene to ethylbenzene depended on the concentration of phenylacetylene still present in solution. Additional experi-



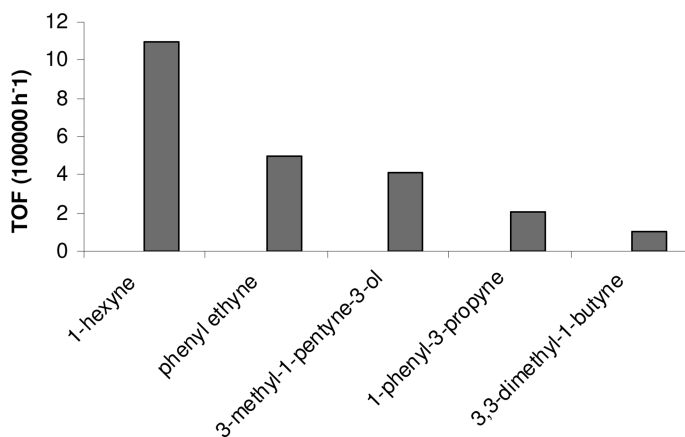
**Scheme 9.8** Semihydrogenation of olefin alcohols with Pd colloids stabilized by a block copolymer polystyrene-poly-4-vinylpyridine.

**Table 9.13** Comparison of colloidal and heterogeneous catalysts in the hydrogenation of 2-butyne-1,4-diol. (Adapted from [89])

Catalyst	Size [nm]	Selectivity [%]	TOF [ $\times 10^{-5} \text{ h}^{-1}$ ]	$\frac{\text{TOF}_{\text{Mt-PVP}}}{\text{TOF}_{\text{Mt-CaCO}_3}}$
Pt/PVP	5.1	96	5.5	
Pt/CaCO <sub>3</sub>	–	83	0.2	27
Rh/PVP	5	96	4.2	
Rh/CaCO <sub>3</sub>	–	85	0.1	42
Ru/PVP	4.8	95.2	5.1	
Ru/CaCO <sub>3</sub>	–	75	0.14	36
Ni/PVP	9.4	99	0.1	
Ni/C	–	65	0.01	10
Pd/PVA	5.7	99	5	–
Pd/PMVE	5.4	89.2	5.2	–
Pd/PVP	5	91.1	5.7	
Pd/CaCO <sub>3</sub>	–	83	0.15	38

ments conducted in the presence of phosphine showed that the amount of styrene increased while the formation of ethylbenzene versus styrene decreased.

Colloidal catalysts in alkyne hydrogenation are widely used in conventional solvents, but their reactivity and high efficiency were very attractive for application in scCO<sub>2</sub>. This method, which is based on colloidal catalyst dispersed in scCO<sub>2</sub>, yields products of high purity at very high reactions rates. Bimetallic Pd/Au nanoparticles (Pd exclusively at the surface, while Au forms the cores) embedded in block copolymer micelles of polystyrene-block-poly-4-vinylpyridine



**Fig. 9.2** TOF-values calculated at 50% conversion in the hydrogenation of various alkynes with a [substrate]/[Pd] ratio near 6500. (Adapted from [91])



were reported in highly efficient single-phase hydrogenation of alkynes in  $\text{scCO}_2$  [91]. Several substrates, including 1-hexyne, 3-methyl-1-pentyne-3-ol, 3,3-dimethyl-1-butyne, phenyl ethyne and 1-phenyl-3-propyne, were investigated at a hydrogen pressure of 15 bar,  $50^\circ\text{C}$  and a  $\text{CO}_2$  pressure of 150 bar (Fig. 9.2).

According to the hydrogen pressure and substrate/Pd ratio, a TOF up to  $4 \times 10^6 \text{ h}^{-1}$  was observed for the hydrogenation of 1-hexyne, this being the highest TOF ever reported for alkyne hydrogenation.

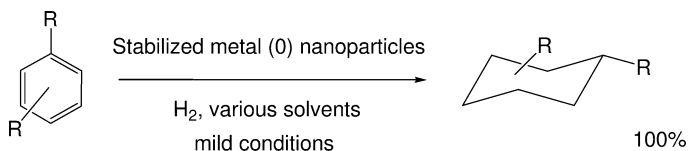
## 9.5 Arene Hydrogenation

In most cases, the industrial hydrogenation of benzene and derivative compounds is performed using heterogeneous catalysis [92, 93]. In many cases (if not the majority) these systems require drastic conditions (high hydrogen pressure and/or temperature), but the use of nanoparticles under mild conditions has received an increasing amount of attention since some homogeneous catalysts were shown to be micro- or nano-heterogeneous [4–6]. Recent progress [94, 95] in the complete catalytic hydrogenation of monocyclic aromatic compounds by noble metal (0) nanoparticles such as Pt, Rh, Ru or Ir in various liquid media has been described in the literature (Scheme 9.9).

In this strategic research area, significant results based on a critical combination of various parameters were obtained by several catalytic systems [94]. Three parameters seem to be highly important:

- the stabilizing agent, which may be either one of PVP, polyoxoanion, surfactant or ionic liquids;
- the nature of the precursor: metal salts or organometallic compounds; and
- the type of the catalytic system: monophasic (organic) or biphasic liquid–liquid (organic/organic and water/organic) media.

Ammonium salts are commonly used to stabilize aqueous colloidal suspensions of nanoparticles. The first such example was reported in 1983–84 by Januszkiwicz and Alper [96, 97], who described the hydrogenation of several benzene derivatives under 1 bar  $\text{H}_2$  and biphasic conditions starting with  $[\text{RhCl}(\text{1,5-hexadiene})_2]$  as the metal source and with tetraalkylammonium bromide as a stabilizing agent. Some ten years later, Lemaire and coworkers investigated the *cis*/



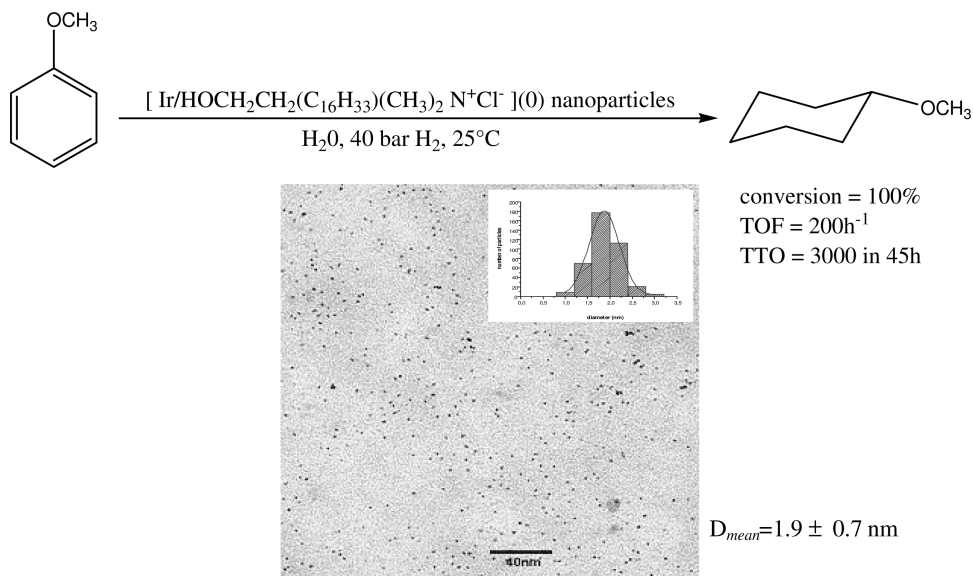
**Scheme 9.9** Total hydrogenation of monocyclic arene compounds by various zerovalent noble-metal nanoparticles.

*trans* selectivity in the hydrogenation of methylanisole and cresol derivatives. Rhodium colloids in the 2- to 3-nm size range were obtained from rhodium trichloride in the presence of tricaprylylmethylammonium chloride salt or triocetylamine. A Total Turn Over (TTO) of 40 in 24 h was reported for the hydrogenation of 2-methylanisole, and the *cis* compound was formed with selectivities exceeding 97% [98]. These authors also observed a partial hydrogenolysis of the methoxy group (10%). Similarly, James and coworkers used tetrabutylammonium salts to stabilize rhodium and ruthenium nanoparticles. Several substrates containing the 4-propylphenol fragment were hydrogenated in biphasic media and under various conditions (20–100 °C, 1–50 bar H<sub>2</sub>). The best results were obtained for the hydrogenation of 2-methoxy-4-propylphenol by ruthenium nanoparticles with a TTO of 300 in 24 h [99–101].

In 1999, the group of Roucoux succeeded in the synthesis of aqueous suspensions of rhodium(0) colloids by reducing RhCl<sub>3</sub>·3H<sub>2</sub>O with NaBH<sub>4</sub> in the presence of surfactants which provide an electrosterical stabilization. Nanoparticles stabilized by *N,N*-dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium salts (counteranion: Br, Cl, I, CH<sub>3</sub>SO<sub>3</sub>, BF<sub>4</sub>) are well-defined with a mean size of 2–3 nm. Various mono-, di-substituted and/or functionalized arene derivatives are hydrogenated, with TOFs up to 200 h<sup>-1</sup>, in pure biphasic liquid–liquid (water/substrate) media at 20 °C and 1 bar H<sub>2</sub>. The hydrogenation of anisole is observed with a TOF of 4000 h<sup>-1</sup> under 40 bar H<sub>2</sub>. The nanocatalyst could be separated by simple decantation and reused in successive hydrogenation reactions. Significant results have been obtained in the hydrogenation of anisole, with 2000 TTO in 37 h [14,15]. In the same manner, the efficient hydrogenation of various benzene compounds in aqueous media at room temperature and under 40 bar H<sub>2</sub> has also been described by using similar reusable surfactant-protected iridium(0) nanoparticles [102]. In all cases, the conversion is complete after a few hours. A TTO of 3000 was obtained for anisole hydrogenation in 45 h. TEM observations showed the particles to be monodispersed, with an average diameter of 1.9±0.7 nm (Scheme 9.10). Selective hydrogenation of di-substituted benzenes such as xylene, methylanisole, and cresol was also observed with these aqueous suspensions of rhodium(0) and iridium(0) nanoparticles. In all cases, the *cis*-compound is the major product (>80%). The *cis/trans* ratio decreases with the position of the substituents *ortho* > *meta* > *para*, but the nature of the metal does not seem important with this surfactant-stabilized system [14, 102].

Similar surfactant-stabilized colloidal systems have been reported by Albach and Jautelat, who prepared aqueous suspensions of Ru, Rh, Pd, Ni nanoparticles and bimetallic mixtures stabilized by dodecyldimethylammonium propane-sulfonate [103]. Benzene, cumene and isopropylbenzene were reduced in biphasic conditions under various conditions at 100–150 °C and 60 bar H<sub>2</sub>, and TTO up to 250 were obtained.

The immobilization of metal nanoparticles with a water-soluble polymeric material such as PVP has also been described. The groups of Choukroun and Chaudret have described the hydrogenation of benzene in a biphasic mixture with PVP-protected native Rh nanoparticles synthesized from the organometal-



**Scheme 9.10** Hydrogenation of anisole by reusable surfactant-stabilized Ir(0) colloids in water. TEM micrograph and size distribution of Ir(0). (Adapted from [102].)

lic complex  $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$  [90]. The presence of soluble Rh nanoparticles with sizes in the 2- to 3-nm range was confirmed by TEM. In water/benzene biphasic conditions at 30 °C and under 7 bar  $\text{H}_2$ , complete benzene hydrogenation is observed at a substrate:catalyst ratio of 2000 after 8 h, giving rise to a TOF of 675  $\text{h}^{-1}$  (related to  $\text{H}_2$  consumed).

Details of a similar polymer-stabilized colloidal system were published by James and coworkers [104]. Rhodium colloids are produced by reducing  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  with ethanol in the presence of PVP. The monophasic hydrogenation of various substrates such as benzyl acetone and 4-propylphenol and benzene derivatives was performed under mild conditions (25 °C, 1 bar  $\text{H}_2$ ). The nanoparticles are poorly characterized and benzyl acetone is reduced, with 50 TTO in 43 h.

Recently, Dupont and coworkers described the use of room-temperature imidazolium ionic liquids for the formation and stabilization of transition-metal nanoparticles. The potential interest in the use of ionic liquids is to promote a biphasic organic–organic catalytic system for a recycling process. The mixture forms a two-phase system consisting of a lower phase which contains the nanocatalyst in the ionic liquid, and an upper phase which contains the organic products. Rhodium and iridium [105], platinum [73] or ruthenium [74] nanoparticles were prepared from various salts or organometallic precursors in dry 1-butyl-3-methylimidazolium hexafluorophosphate ( $\text{BMI PF}_6$ ) ionic liquid under hydrogen pressure (4 bar) at 75 °C. Nanoparticles with a mean diameter of 2–3 nm

were isolated by centrifugation. The isolated colloids could be used as solids (heterogeneous catalyst), in acetone solution (homogeneous catalyst), or re-dispersed in BMI PF<sub>6</sub> (biphasic system) for benzene hydrogenation studies. Iridium and rhodium nanoparticles have also been studied in the hydrogenation of various aromatic compounds [105]. In all cases, total conversions were not observed in BMI PF<sub>6</sub>. A comparison between Ir(0) and Rh(0) nanoparticles shows that iridium colloids are much more active for the benzene hydrogenation in biphasic conditions, with TOFs of 50 h<sup>-1</sup> and 11 h<sup>-1</sup>, respectively, and 24 h<sup>-1</sup> and 5 h<sup>-1</sup> for *p*-xylene reduction at 75 °C and under 4 bar H<sub>2</sub>. The best results were obtained with platinum nanoparticles prepared from simple decomposition of Pt<sub>2</sub>(dba)<sub>3</sub> in heterogeneous (solventless) conditions with a TOF of 28 h<sup>-1</sup> for 100% conversion. The authors reported that the TOF dramatically decreased in biphasic liquid–liquid condition (BMI PF<sub>6</sub>) to 11 h<sup>-1</sup> at 46% conversion, justifying the absence of recycling studies with this substrate [73]. Finally, Dupont and coworkers have described the preparation of Ru(0) nanoparticles by H<sub>2</sub> reduction of the organometallic precursor Ru(COD)(COT) in BMI PF<sub>6</sub>, a room-temperature ionic liquid, with hydrogen pressure [74]. These nanoparticles are efficient catalysts for the complete hydrogenation of benzene (TOF = 125 h<sup>-1</sup>) under solventless conditions (heterogeneous catalyst). In a biphasic system, the authors observed a partial conversion in BMI PF<sub>6</sub> with a modest TOF of 20 h<sup>-1</sup> at 73% conversion in the benzene hydrogenation.

More recently, Dupont and coworkers studied the impact of the steric effect in the hydrogenation of monoalkylbenzenes by zerovalent nanoparticles (Ir, Rh, Ru) in the ionic liquid BMI PF<sub>6</sub>. The results, when compared with those obtained with the classical supported heterogeneous catalysts, showed a relationship between the reaction constants and the steric factors [106].

Finally, these particles generated in ionic liquids are efficient nanocatalysts for the hydrogenation of arenes, although the best performances were not obtained in biphasic liquid–liquid conditions. The main importance of this system should be seen in terms of product separation and catalyst recycling. An interesting alternative is proposed by Kou and coworkers [107], who described the synthesis of a rhodium colloidal suspension in BMI BF<sub>4</sub> in the presence of the ionic copolymer poly[(*N*-vinyl-2-pyrrolidone)-*co*-(1-vinyl-3-butylimidazolium chloride)] as protective agent. The authors reported nanoparticles with a mean diameter of ca. 2.9 nm and a TOF of 250 h<sup>-1</sup> in the hydrogenation of benzene at 75 °C and under 40 bar H<sub>2</sub>. An impressive TTO of 20 000 is claimed after five total recycles.

An alternative approach to stabilize nanoparticles is to use polyoxoanions (see Scheme 9.5). Finke and coworkers described polyoxoanion- and ammonium-stabilized rhodium zerovalent nanoclusters for the hydrogenation of classical benzene compounds [95, 108]. This organometallic approach allows reproducible preparation of stable nanoparticles starting from a well-defined complex in terms of composition and structure (see Section 9.3.5).

The polyoxoanion-stabilized Rh(0) nanoclusters were investigated in anisole hydrogenation [6,95]. The catalytic reactions were carried out in a single phase

using a propylene carbonate solution under mild conditions (22 °C, 3.7 bar H<sub>2</sub>). Under these standard conditions, anisole hydrogenation with a substrate:catalyst (S:Rh) ratio of 2600 was performed in 120 h, giving rise to a TTO of 1500 ± 100. The authors observed that the addition of proton donors such as HBF<sub>4</sub>·Et<sub>2</sub>O or H<sub>2</sub>O increased the catalytic activity, and reported 2600 TTO for complete hydrogenation in 144 h at 22 °C and 3.7 bar H<sub>2</sub> with a ratio HBF<sub>4</sub>·Et<sub>2</sub>O:Rh of 10. A black precipitate of bulk Rh(0) is visible at the end of the reaction as a result of the destabilization of nanoclusters due to the interaction of H<sup>+</sup> or H<sub>2</sub>O with the basic P<sub>2</sub>W<sub>15</sub>Nb<sub>3</sub>O<sub>62</sub><sup>9-</sup> polyoxoanion.

During the past decade, a variety of stabilized systems based on transition-metal nanoparticles has been seriously investigated, and better lifetimes and activities for the total hydrogenation of monocyclic arene derivatives under mild conditions have been reported. New catalytic systems have been described in various media such as supercritical fluids [109], and these represent a promising area of future research. Several recent investigations have shown modest, but promising, results in partial or selective arene hydrogenation with well-defined colloids [94]. In the future, the partial hydrogenation of arene derivatives into cyclohexene or cyclohexadiene compounds should be highlighted as they are key intermediates in organic synthesis.

The process developed by Asahi Chemical Industry in Japan [110], and performed in a tetraphasic system combining gas, oil, water and ruthenium particles with an average diameter of 20 nm, is a significant milestone in this area. The selectivity is very high and a yield of 60% in cyclohexene is obtained with this “bulk” ruthenium catalyst in the presence of zinc as co-catalyst at 150 °C and under 50.4 bar of H<sub>2</sub>. The cyclohexene produced by this process is used as a feedstock for caprolactam.

At present, the efficient partial hydrogenation of benzene and its derivatives has been rarely described with well-defined soluble nanoparticles catalysts. Nonetheless, this remains an interesting area for research, with promising future applications.

## 9.6

### Hydrogenation of Compounds with C=O Bonds

Several reports have been made of the hydrogenation of compounds bearing C=O bonds by colloidal catalytic systems.

In 1996, Liu et al. reported the selective hydrogenation of cinnamaldehyde, an  $\alpha,\beta$ -unsaturated aldehyde, to cinnamyl alcohol, an  $\alpha,\beta$ -unsaturated alcohol, by means of PVP-protected Pt/Co bimetallic colloids prepared by the polyol process [111]. The colloids were obtained as a dark-brown homogeneous dispersion in a mixture of ethylene glycol and diethylene glycol, and characterized by TEM and XRD. These authors prepared different samples of nanoparticles with Pt:Co ratios of 3:1 and 1:1, the mean diameters of which measured 1.7 and 2.2 nm, respectively. These colloidal systems were also compared with the single metal-

based colloids Pt/PVP and Co/PVP. The catalytic tests were carried out under a  $H_2$  pressure of 4 MPa at 333 K in EtOH. While Pt/PVP and Co/PVP colloids gave low activity and selectivity, bimetallic colloids exhibited interesting behavior, with the Pt:Co/PVP (3:1) system being the most interesting. Selectivity in cinnamyl alcohol up to 99.8% was indeed obtained with colloid Pt:Co (3:1) with very good conversions (up to 96.2%). It was observed that activity and selectivity could be affected by the presence of added water or NaOH in the reaction mixture. These results are of interest as it is a difficult task to reduce only the C=O bond when it is conjugated to a C=C double bond, with almost all metal catalysts readily reducing the C=C double bond. These results also showed that the colloids were stable enough for catalytic hydrogenation reaction at elevated temperature and pressure.

Another example from Liu's team in this field concerns the selective hydrogenation of citronellal to citronellol by using a Ru/PVP colloid obtained by  $NaBH_4$  reduction method [112]. This colloid contains relatively small particles with a narrow size distribution (1.3 to 1.8 nm by TEM), whereas the metallic state of Ru was confirmed by XPS investigation. This colloid exhibited a selectivity to citronellol of 95.2% with a yield of 84.2% (total conversion 88.4%), which represented a good result for a monometallic catalyst.

Gin and coworkers have presented an original strategy for the synthesis of Pd nanoparticles with both good stability and catalytic activity in benzaldehyde hydrogenation by using a cross-linked lyotropic liquid crystal (LLC) assembly as an organic template (Fig. 9.3) [113]. Incorporation of Pd atoms has been performed by ion exchange on the cross-linked inverted hexagonal phase of the sodium salt with an acetonitrile solution of dichloro(1,5-cyclooctadiene)palladium II complex. The Pd-(II)-LLC composite was treated with dihydrogen to afford spherical Pd nanoparticles of 4–7 nm mean size dispersed in the polymer ma-

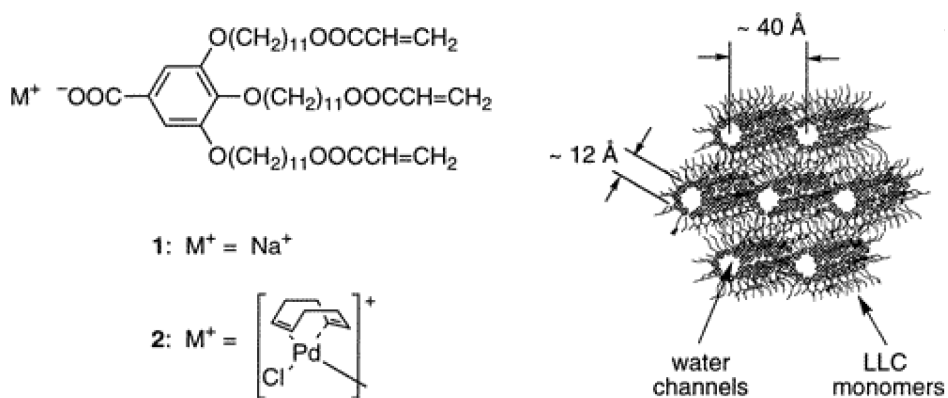


Fig. 9.3 The structure of LLC monomers, 1 and 2, and the inverted hexagonal phase. (Reprinted with the permission of the American Chemical Society [113])

trix. The benzaldehyde hydrogenation was carried out under 1 bar H<sub>2</sub> and 60 °C, and a 98% yield of benzylalcohol was observed after 3 h of reaction.

Pertici et al. described the synthesis of ruthenium nanoparticles on polyorganophosphazenes (PDMP) as stabilizing polymers [114]. The synthesis method consisted of the decomposition of a THF solution of the organometallic Ru( $\eta^4$ -COD)( $\eta^6$ -COT) complex at 45 °C under dihydrogen atmosphere in the presence of various polyorganophosphazenes. This procedure gave rise to new materials in which small ruthenium clusters were bound to the arene groups of the polymers. High-resolution TEM analysis revealed well-dispersed and very small nanoparticles of 1.55±0.5 nm mean size in the polymer matrix. These materials could be purified as fine powders containing 5 wt.% of Ru, the dispersion of which could be easily obtained in organic solvent such as ethanol or THF, or in water, allowing their use as homogeneous catalysts. The catalytic experiments were carried out under mild conditions (25 °C, 1 bar H<sub>2</sub>) in ethanol, THF or water as solvent. Olefin and ketone hydrogenations were performed. A wide range of carbonyl compounds has been tested such as cyclohexanone, ethyl

**Table 9.14** Hydrogenation of ketones with Ru/PDMP at atmospheric hydrogen pressure and 25 °C. (Reprinted with the permission of Elsevier [114])

Substrate <sup>a)</sup>	Solvent	Phase <sup>b)</sup>	Time [h]	Product <sup>c)</sup> [%]	TOF <sup>d)</sup>
Cyclohexanone	Ethanol	Hom	10	Cyclohexanol (100)	10
Ethyl acetoacetate	Ethanol	Hom	24	Ethyl 3-hydroxybutyrate (100)	4.2
Ethyl pyruvate	Ethanol	Hom	6	Ethyl lactate (100)	16.6
Pyruvic acid	Ethanol	Hom	8	Lactic acid (100) <sup>e)</sup>	12.5
Acetophenone	Ethanol	Hom	96	1-Phenylethanol (100)	1
Pyruvic acid	Water	Hom	7	Lactic acid (100) <sup>e)</sup>	14.3
Cyclohexanone <sup>f)</sup>	Ethanol	Hom	30	Cyclohexanol (100)	10
Ethyl acetoacetate <sup>f)</sup>	Ethanol	Hom	6	Ethyl 3-hydroxybutyrate (100)	3.3
Ethyl pyruvate <sup>f)</sup>	Ethanol	Hom	10	Ethyl lactate (100)	16.6
Pyruvic acid <sup>f)</sup>	Ethanol	Hom	8	Lactic acid (100) <sup>e)</sup>	12.5
Acetophenone <sup>f)</sup>	Ethanol	Hom	96	1-Phenylethanol (100)	1
Pyruvic acid <sup>f)</sup>	Water	Hom	7	Lactic acid (100) <sup>e)</sup>	14.3
Cyclohexanone	THF	Het	10	Cyclohexanol (30)	3
Ethyl acetoacetate	THF	Het	30	Ethyl 3-hydroxybutyrate (20)	0.7
Ethyl pyruvate	THF	Het	6	Ethyl lactate (20)	3
Acetophenone	THF	Het	96	1-Phenylethanol (20)	0.2

a) Substrate (13 mmol); catalyst Ru on PDMP (5 wt.% Ru), 0.26 g (0.13 mg atoms Ru); solvent, 15 mL.

b) Hom: homogeneous phase; Het: heterogeneous phase.

c) Composition determined by GLC analysis.

d) Moles converted substrate per gram-atom ruthenium h<sup>-1</sup>.

e) Composition determined by <sup>1</sup>H-NMR spectroscopy.

f) Catalyst recovered from runs 1–6, respectively, and reused.

acetoacetate, ethyl pyruvate and pyruvic acid as examples of aliphatic carbonyl compounds, and acetophenone as an example of ketone bearing an aryl group. All carbonyl compounds were quantitatively reduced to the corresponding alcohols (Table 9.14). The catalysts could be reused after precipitation with a non-solvent.

A HRTEM study showed these catalysts to be more resistant towards agglomeration, as only a low degree of aggregation was noted after dissolution and precipitation of the catalysts. However, this slight agglomeration did not lead to catalyst deactivation. Finally, a catalytic study of a Ru/poly[bis(aryloxy)]phosphazene system indicated that the structure of the side chain of the support had considerable influence on the activity of the deposited metal, providing the possibility of modifying the catalytic activity by changing the support structure [114].

The group of Dupont has described the use of ionic liquids for the formation and stabilization of various metal nanoparticles and their application in hydrogenation reactions. In a report concerning the use of Ir(0) nanoparticles (mean diameter  $2.1 \pm 0.3$  nm) prepared by reduction with molecular hydrogen (4 bar) of  $[\text{Ir}(\text{COD})\text{Cl}]_2$  (COD=1,5-cyclooctadiene) dissolved in BMI  $\text{PF}_6$  ionic liquid at  $75^\circ\text{C}$ , it was mentioned that the solvent, acetone, used for the “homogeneous” hydrogenation reaction of benzene ( $75^\circ\text{C}$ , 4 bar  $\text{H}_2$ ) is also hydrogenated, even in the early stages of the reaction [115]. These nanoparticles could be isolated by centrifugation and characterized by TEM and XRD. The authors also reported the hydrogenation of acetophenone. Under “solventless” conditions, they observed the formation not only of 1-cyclohexylethanol but also of ethylcyclohexane, the hydrogenolysis product in a high yield (up to 42%). It was concluded that this result suggested a “heterogeneous” behavior of the Ir(0) nanoparticles in terms of active sites. On pursuing these investigations, it was found that such Ir(0) nanoparticles constitute an efficient and recyclable catalyst for the “solventless” or biphasic hydrogenation of various cyclic and acyclic ketones un-

**Table 9.15** Hydrogenation of various carbonyl compounds by Ir(0) nanoparticles in solventless conditions ([substrate]/[Ir] ratio=250,  $75^\circ\text{C}$ , 4 bar). (Adapted from [116])

Substrate	Product	Time [h]	Yield [%] <sup>a)</sup>	TOF <sup>b)</sup> [ $\text{h}^{-1}$ ]
Benzaldehyde	Phenylmethanol	15	100	17
Cyclopentanone	Cyclopentanol	4	100 <sup>c)</sup>	62.5
2-Pentanone	2-Pentanol	2.5	96	96
4-Methyl-2-pentanone	4-Methyl-2-pentanol	2.5	96	96
3-Pentanone	3-Pentanol	3.7	100	68
Ethylpyruvate	Ethyl-lactate	2.5	98	98
Acetone	2-Propanol	2.0	95	119

a) Conversions determined by GLC.

b)  $\text{Mol ketone mol}^{-1} \text{ iridium h}^{-1}$ .

c) Products obtained were cyclopentanol and bicyclopentyl ether (12%).



der mild conditions (Table 9.15) after optimization of the reaction conditions with cyclohexanone [116]. In the case of ketones containing aromatic cycles, a tendency for the selective hydrogenation of the aromatic ring was observed. The method was also applied to the hydrogenation of benzaldehyde.

## 9.7 Enantioselective Hydrogenation

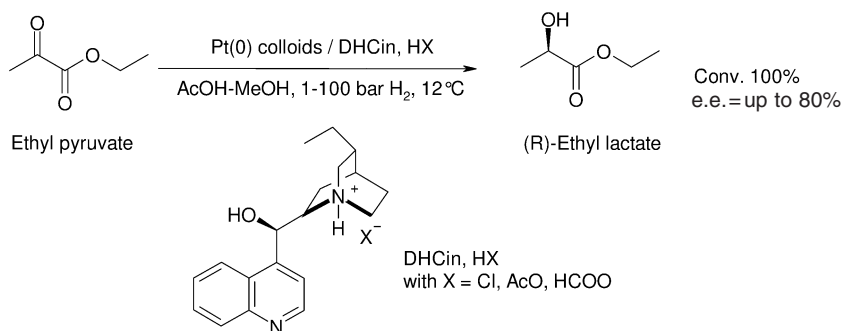
The enantioselective hydrogenation of prochiral substances bearing an activated group, such as an ester, an acid or an amide, is often an important step in the industrial synthesis of fine and pharmaceutical products. In addition to the hydrogenation of  $\beta$ -ketoesters into optically pure products with Raney nickel modified by tartaric acid [117], the asymmetric reduction of  $\alpha$ -ketoesters on heterogeneous platinum catalysts modified by cinchona alkaloids (cinchonidine and cinchonine) was reported for the first time by Orito and coworkers [118–121]. Asymmetric catalysis on solid surfaces remains a very important research area for a better mechanistic understanding of the interaction between the substrate, the modifier and the catalyst [122–125], although excellent results in terms of enantiomeric excesses (up to 97%) have been obtained in the reduction of ethyl pyruvate under optimum reaction conditions with these Pt/cinchona systems [126–128].

Supported palladium and platinum modified by chiral compounds are largely used as pure heterogeneous hydrogenation catalysts. However, recent studies have been performed starting with catalysts of colloidal nature and particles with dimensions of only a few nanometers. Their development continues to attract substantial interest for three main reasons:

- The elimination of the support such as  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ , zeoliths and of its influences.
- The possibility of obtaining size- and shape-controlled nanoparticles, thereby giving efficient activities.
- The possibility of adapting chiral molecules as inducer or stabilizer (form and amount) for better selectivities.

The concept of using colloids stabilized with chiral ligands was first applied by Bönnemann to hydrogenate ethyl pyruvate to ethyl lactate with Pt colloids. The nanoparticles were stabilized by the addition of dihydrocinchonidine salt (DHCin, HX) and were used in the liquid phase or adsorbed onto activated charcoal and silica [129, 130]. The molar ratio of platinum to dihydrocinchonidine, which ranged from 0.5 to 3.5 during the synthesis, determines the particle size from 1.5 to 4 nm and contributes to a slight decrease in activity ( $\text{TOF}=1 \text{ s}^{-1}$ ). In an acetic acid/MeOH mixture and under a hydrogen pressure up to 100 bar, the (*R*)-ethyl lactate was obtained with optical yields of 75–80% (Scheme 9.11).

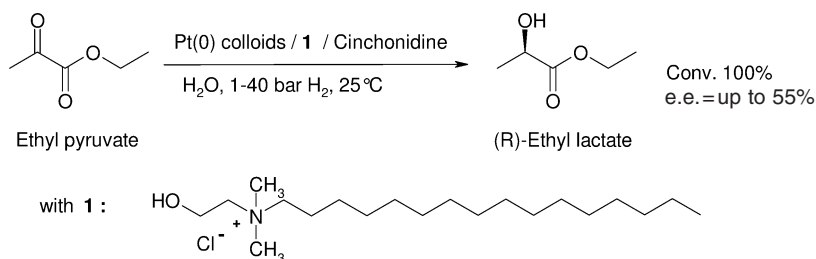
Several mechanistic investigations concerning the hydrogenation of pyruvate derivatives (ethyl or methyl esters) were performed with platinum, rhodium and



**Scheme 9.11** Enantioselective hydrogenation of ethyl pyruvate with platinum colloids stabilized by protonated-dihydrocinchonidine.

iridium nanoparticles stabilized by PVP. In all cases, nanoparticles of size range 2 to 4 nm were modified by cinchonidine or quinine [127, 131–135]. The Pt/PVP catalyst hydrogenated ethyl pyruvate, with ee-values up to 92%, and methyl pyruvate with ee-values up to 98%, depending upon the nanoparticle size. The best results were obtained in acetic acid. The asymmetric hydrogenation of trifluoroacetophenone and  $\alpha$ -diketones such as 2,3-butanedione and 3,4-hexanedione was also investigated using finely dispersed PVP-stabilized Pt nanoparticles modified with cinchonidine, and ee-values of up to 30% were reported, according to the solvent [136, 137]. Similar results (ee 30%) were described with solvent-stabilized Pt and Pd nanoparticles prepared by the metal vapor synthesis route for the enantioselective hydrogenation of ethyl pyruvate [138].

Recently, platinum nanoparticles protected by *N,N*-dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium chloride salt and modified with cinchonidine were investigated in the enantiomeric hydrogenation of ethyl pyruvate in pure biphasic liquid–liquid (water/substrate) media at room temperature [139]. For the first time, the aqueous phase containing Pt(0) nanocatalysts with an average size of 2.5 nm could be reused for successive hydrogenations, and with a total conversion of activity and enantioselectivity in (*R*)-(+)-ethyl lactate up to 55% (Scheme 9.12).



**Scheme 9.12** Reusable aqueous suspension of Pt nanoparticles for enantioselective hydrogenation of ethyl pyruvate.

**Table 9.16** Comparison of stabilized nanoparticle systems modified with cinchonidine for the hydrogenation of various  $\alpha$ -ketoesters and  $\alpha$ -diketones.

Catalyst	Substrate	Solvent	Conversion [%]	Temp. [°C]	PH <sub>2</sub> [bar]	ee [%] (config.)	Reference(s)
Pt-PVP	Methyl pyruvate <sup>a)</sup>	AcOH	100	25	40	97.6 (R)	127, 135
Pt-PVP	Ethyl pyruvate <sup>b)</sup>	AcOH	100	25	40	93.8 (R)	127, 135
Pt-PVP	<i>n</i> -propyl pyruvate <sup>b)</sup>	AcOH	100	25	40	95.6 (R)	135
Pt-PVP	<i>Iso</i> -propyl pyruvate <sup>b)</sup>	AcOH	58.5	25	40	77.1 (R)	135
Pt-PVP	<i>n</i> -butyl pyruvate <sup>b)</sup>	AcOH	86.7	25	40	90.5 (R)	135
Pt-PVP	<i>Iso</i> -butyl pyruvate <sup>b)</sup>	AcOH	95.5	25	40	93.1 (R)	135
Pt-PVP	Methyl pyruvate <sup>c)</sup>	EtOH	61.3	25	40	84.7 (R)	127
Pt-DHCin,HX	Ethyl pyruvate <sup>d)</sup>	AcOH/MeOH	100	19	1–100	75–80 (R)	129, 130
Pt-MEK	Ethyl pyruvate <sup>e)</sup>	MEK	100	25	70	25 (R)	138
Pt-MMK	Ethyl pyruvate <sup>f)</sup>	MMK-H <sub>2</sub> O	100	25	70	36 (S)	138
Pt-HEA16Cl	Ethyl pyruvate <sup>g)</sup>	H <sub>2</sub> O	100	25	40	55 (R)	139
Pt/PVP	2,3-Butanedione <sup>h)</sup>	EtOH	95.5	25	40	27.9 (R)	136
Pt/PVP	2,3-Butanedione <sup>h)</sup>	AcOH	92.9	25	40	22.6 (R)	136
Ir-PVP	2,3-Butanedione <sup>h)</sup>	AcOH	80.5	25	40	20.4 (R)	136
Pt/PVP	3,4-Hexanedione <sup>h)</sup>	EtOH	94.9	25	40	18.0 (R)	136
Pt/PVP	3,4-Hexanedione <sup>h)</sup>	AcOH	87.8	25	40	20.6 (R)	136
Pd-MEK-KD1	Ethyl pyruvate <sup>i)</sup>	MEK	13	25	70	29 (R)	138
Rh-PVP	Ethyl pyruvate <sup>j)</sup>	EtOH/THF	100	25	50	42.2 (R)	133
Ir-PVP	Methyl pyruvate <sup>k)</sup>	EtOH	85	20	25	17.0 (R)	134

a) TOF = 1.21 s<sup>-1</sup>.

b) [substrate]/[Pt] ratio = 1600.

c) TOF = 0.76 s<sup>-1</sup>.d) TOF ≈ 1 s<sup>-1</sup>.e) Initial rate = 1025 mmol s<sup>-1</sup> mol<sup>-1</sup><sub>metal</sub>.f) Cinchonine is used as modifier, initial rate = 2253 mmol s<sup>-1</sup> mol<sup>-1</sup><sub>metal</sub>.

g) [substrate]/[Pt] ratio = 400.

h) [substrate]/[Pt] ratio = 1765.

i) Initial rate = 47 mmol s<sup>-1</sup> mol<sup>-1</sup><sub>metal</sub>.j) TOF = 941 h<sup>-1</sup>.k) Average rate = 838 mmol h<sup>-1</sup> g<sup>-1</sup><sub>metal</sub>.

Although several noble-metal nanoparticles have been investigated for the enantiomeric catalysis of prochiral substrates, platinum colloids remain the most widely studied. PVP-stabilized platinum modified with cinchonidine showed ee-values >95%. Several stabilizers have been also investigated such as surfactants, cinchonidinium salts and solvents, and promising ee-values have been observed. Details of a comparison of various catalytic systems are listed in Table 9.16; in one case, the colloid suspension was reused without any loss in enantioselectivity. Clearly, the development of convenient two-phase liquid–liquid systems for the recycling of chiral colloids remains a future challenge.

## 9.8

**Conclusion**

This chapter provides a non-exhaustive overview of the hydrogenation of carbon-carbon double or triple bonds, carbonyl groups and aromatic compounds with colloids as soluble catalysts. The subject, while of crucial importance, is generally not covered in detail in books on homogeneous catalysis, despite several efficient molecular homogeneous complexes having been shown to be precursors of “nanoheterogeneous” catalysts. Such materials, when correctly characterized, constitute an interesting class of both homogeneous and/or heterogeneous catalysts, and the use of colloids is generally seen as being compatible with a variety of reaction media according to the organic- or water-soluble nature of the stabilizers. Colloids can also be adapted for use in biphasic conditions, thereby allowing recovery of the nanocatalysts by simple decantation/filtration, and subsequent recycling. Although stabilized colloids are neither “traditional” nor “routine” catalysts, their performances in some cases – and their potential role as catalysts – is now clearly recognized by the scientific community, and nanoparticle systems represent an interesting compromise between homogeneous and heterogeneous catalytic systems, both in terms of activity and selectivity. Finally, the number of reports related to the use of colloids in catalysis has increased significantly, with interest in colloidal systems limited not only to current hydrogenation reactions but also being indicative of future processes.

**Abbreviations**

$\beta$ -CD	$\beta$ -cyclodextrin
BMI PF <sub>6</sub>	1- <i>n</i> -butyl-3-methylimidazolium hexafluorophosphate
COD	cycloocta-1,5-diene
COT	cycloocta-1,3,5-triene
DLVO	Derjaguin-Landau-Verwey-Overbeek
DTAC	dodecyltrimethylammonium
EDX	electron diffraction X-ray
EXAFS	extended X-ray absorption fine structure
HDA	hexadecylaniline
HRTEM	high-resolution TEM
LLC	lyotropic liquid crystal
NMR	nuclear magnetic resonance
PAA	poly(acrylic acid)
PAMAM	poly(amidoamine)
PDMS- <i>b</i> -PEO	poly(dimethylsiloxane)- <i>b</i> -poly(ethylene oxide)
PEG	polyethylene glycol
PPI	poly(propylene imine)
PS- <i>b</i> -PEO	polystyrene- <i>b</i> -poly(ethylene oxide)
PS- <i>b</i> -PMAA	polystyrene- <i>b</i> -poly(methacrylic acid)

PtBA- <i>b</i> -PCEMA	poly( <i>t</i> -butyl acrylate)- <i>block</i> -poly(2-cinnamoyloxyethyl) methacrylate
PVA	polyvinylalcohol
PVP	polyvinylpyrrolidone
SAED	selected area electron diffraction
SDS	sodium dodecylsulfate
TEM	transmission electronic microscopy
TGA	thermogravimetric analysis
TOF	turnover frequency
THF	tetrahydrofuran
TTO	total turnover
WAXS	wide-angle X-ray scattering
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

## References

- G. Schmid (Ed.), *Nanoparticles. From theory to application*. Wiley-VCH, Weinheim, **2004**.
- D.L. Feldheim, C.A. Foss, Jr. (Eds.), *Metal Nanoparticles: Synthesis, Characterization and Applications*. Marcel Dekker, New York, **2002**.
- A. Roucoux, J. Schulz, H. Patin, *Chem. Rev.* **2002**, *102*, 3757.
- P.J. Dyson, *Dalton Trans.* **2003**, 2964.
- J.A. Widegren, R.G. Finke, *J. Mol. Catal. A Chem.* **2003**, *198*, 317.
- M.C. Hagen, L. Vieille-Petit, G. Laurenczy, G. Suss-Finke, R. Finke, *Organometallics* **2005**, *24*, 1819.
- K. Philippot, B. Chaudret, C. R. *Chimie* **2003**, *6*, 1019.
- J.T.G. Overbeek, in: Goodwin, J.W. (Ed.), *Colloidal Dispersions*. Royal Society of Chemistry, London **1981**, pp. 1–23.
- D.F. Evans, H. Wennerström, in: *The Colloidal Domain*, 2nd edn. Wiley-VCH, New York, **1999**.
- R.J. Hunter, in: *Foundations of Colloid Science*. Oxford University Press, New York **1987**, vol. 1, pp. 316.
- D.H. Napper, in: *Polymeric Stabilization of Colloidal Dispersions*. Academic Press, London, **1983**.
- M. Komiyama, H. Hirai, *Bull. Chem. Soc. Mater.* **1993**, *56*, 2833.
- A. Duteil, R. Queau, B. Chaudret, C. Roucau, J.S. Bradley, *Chem. Mater.* **1993**, *5*, 341.
- J. Schulz, A. Roucoux, H. Patin, *Chem. Eur. J.* **2000**, *6*, 618.
- A. Roucoux, J. Schulz, H. Patin, *Adv. Synth. Catal.* **2002**, *345*, 222.
- L. Manna, S.C. Scher, A.P. Alivisatos, *J. Am. Chem. Soc.* **2000**, *122*, 12700.
- A. Duteil, G. Schmid, W. Meyer-Zaika, *J. Chem. Soc. Chem. Commun.* **1995**, 31.
- A. Rodriguez, C. Amiens, B. Chaudret, M.J. Casanove, P. Lecante, J.S. Bradley, *Chem. Mater.* **1996**, *8*, 1978.
- F. Dassenoy, K. Philippot, T. Ould Ely, C. Amiens, P. Lecante, E. Snoeck, A. Mosset, M.J. Casanove, B. Chaudret, *New J. Chem.* **1998**, *22*, 703.
- S. Chen, K. Kimura, *J. Phys. Chem. B* **2001**, *105*, 5397.
- C. Pan, K. Pelzer, K. Philippot, B. Chaudret, F. Dassenoy, P. Lecante, M.J. Casanove, *J. Am. Chem. Soc.* **2001**, *123*, 7584.
- C.J. Kiely, J. Fink, M. Brust, D. Bethell, D.J. Schiffrin, *Nature* **1998**, *396*, 444.
- G. Schmid, V. Maihack, F. Lantermann, S. Peschel, *J. Chem. Soc. Dalton Trans.* **1996**, 589.
- N. Cordente, M. Respaud, F. Senocq, M.J. Casanove, C. Amiens, B. Chaudret, *Nano Lett.* **2001**, *1*, 565.

- 25 G. Schmid, S. Emde, V. Maihack, W. Meyer-Zaika, S. Peschel, *J. Mol. Catal. A Chem.* **1996**, *107*, 95.
- 26 K. Soulantica, A. Maisonnat, M. C. Fromen, M. J. Casanove, P. Lecante, B. Chaudret, *Angew. Chem. Int. Ed.* **2001**, *38*, 3736.
- 27 M. Gomez, K. Philippot, V. Collière, P. Lecante, G. Muller, B. Chaudret, *New J. Chem.* **2003**, *27*, 114.
- 28 O. Vidoni, K. Philippot, C. Amiens, B. Chaudret, O. Balmes, J. O. Malm, J. a O. Bovin, F. Senocq, M. J. Casanove, *Angew. Chem. Int. Ed.* **1999**, *38*, 3736.
- 29 K. Pelzer, K. Philippot, B. Chaudret, *Z. Phys. Chem.* **2003**, *217*, 1539.
- 30 K. Pelzer, O. Vidoni, K. Philippot, B. Chaudret, V. Colliere, *Adv. Funct. Mater.* **2003**, *13*, 118.
- 31 Y. Wang, J. Ren, K. Deng, L. Gui, Y. Tang, *Chem. Mater.* **2000**, *12*, 1622.
- 32 H. Hirai, *J. Macromol. Sci. Chem.* **1979**, *A13(5)*, 633.
- 33 Y. Shiraishi, M. Nakayama, E. Takagi, T. Tominaga, N. Toshima, *Inorg. Chim. Acta* **2000**, *300–302*, 964.
- 34 N. Toshima, K. Kushihashi, T. Yonezawa, H. Hirai, *Chem. Lett.* **1989**, 1769.
- 35 N. Toshima, T. Yonezawa, M. Harada, K. Asakura, Y. Iwasawa, *Chem. Lett.* **1990**, 815.
- 36 N. Toshima, T. Yonezawa, K. Kushihashi, *J. Chem. Soc. Faraday Trans.* **1993**, *89(14)*, 2537.
- 37 M. Harada, K. Asakura, N. Toshima, *J. Phys. Chem.* **1993**, *97*, 5103.
- 38 N. Toshima, Y. Wang, *Langmuir* **1994**, *10*, 4574.
- 39 N. Toshima, *Fine Particles Science and Technology* **1996**, 371.
- 40 A. Borsla, A. M. Wilhelm, H. Delmas, *Catal. Today* **2001**, *66*, 389.
- 41 A. B. R. Mayer, J. E. Mark, *Polym. Mater. Sci. Eng.* **1995**, *73*, 220.
- 42 A. B. R. Mayer, J. E. Mark, *Polymer Bulletin* **1996**, *37*, 683.
- 43 A. B. R. Mayer, J. E. Mark, *Macromol. Rep.* **1996**, *A33(suppl. 7/8)*, 451.
- 44 A. B. R. Mayer, J. E. Mark, *J. Polym. Sci. Part A: Polym. Chem.* **1997**, *35(15)*, 3151.
- 45 A. B. R. Mayer, J. E. Mark, *Polymers Preprints* **1996**, *37(1)*, 459.
- 46 A. B. R. Mayer, J. E. Mark, R. E. Morris, *Polym. J.* **1998**, *30(3)*, 197.
- 47 Z. Lu, G. Liu, H. Phillips, J. M. Hill, J. Chang, R. A. Kydd, *Nano Lett.* **2001**, *1(12)*, 683.
- 48 M. V. Seregina, L. M. Bronstein, O. A. Platonova, D. M. Chernyshov, P. M. Valtetsky, *Chem. Mater.* **1997**, *9*, 923.
- 49 C.-W. Chen, D. Tano, M. Akashi, *J. Colloid Interface Sci.* **2000**, *225*, 349.
- 50 C.-W. Chen, M. Akashi, *Polym. Adv. Technol.* **1999**, *10*, 127.
- 51 M. Adlim, M. A. Bakar, K. Y. Liew, J. Ismail, *J. Mol. Catal. A: Chem.* **2004**, *212*, 141.
- 52 B. P. S. Chauhan, J. S. Rathore, T. Bandoo, *J. Am. Chem. Soc.* **2004**, *126*, 8493.
- 53 J. F. Cieben, R. E. Cohen, A. Duran, *Mater. Sci. Eng.* **1999**, *C7*, 45.
- 54 R. M. Crooks, V. Chechik, B. I. Lemon, III, L. Sun, L. K. Yeung, M. Zhao, in: D. L. Feldheim, C. A. Foss, Jr. (Eds.), *Metal Nanoparticles: Synthesis, Characterization and Applications*. Marcel Dekker, New York, **2002**, pp. 262.
- 55 R. M. Crooks, M. Zhao, L. Sun, V. Chechik, L. K. Yeung, *Acc. Chem. Res.* **2001**, *34(3)*, 181.
- 56 R. M. Crooks, Y. Niu, *C. R. Chimie* **2003**, *6*, 1049.
- 57 Y.-M. Chung, H.-K. Rhee, *Catal. Lett.* **2003**, *85(3/4)*, 159.
- 58 Y.-M. Chung, H.-K. Rhee, *J. Mol. Catal. A: Chem.* **2003**, *206*, 291.
- 59 M. Ooe, M. Murata, T. Mizugaki, K. Ebitalani, K. Kaneda, *NanoLett.* **2002**, *2(9)*, 999.
- 60 N. Toshima, T. Takahashi, H. Hirai, *Chemistry Lett.* **1985**, 1245.
- 61 C. Larpent, E. Bernard, F. Brisse-le-Menn, H. Patin, *J. Mol. Catal. A: Chem.* **1997**, *116*, 277.
- 62 N. A. Dhas, A. Gedanken, *J. Mater. Chem.* **1999**, *8(2)*, 445.
- 63 J. D. Aiken, III, R. G. Finke, *J. Mol. Catal. A: Chem.* **1996**, *114*, 29.
- 64 J. D. Aiken, III, R. G. Finke, *Chem. Mater.* **1999**, *11*, 1035.
- 65 J. D. Aiken, III, R. G. Finke, *J. Am. Chem. Soc.* **1999**, *121*, 8803.
- 66 S. Mandal, P. R. Selvakannan, D. Roy, R. V. Chaudhari, M. Sastry, *Chem. Commun.* **2002**, 3002.

- 67 I. P. Stoolyarov, Y. V. Gaugash, G. N. Kryukova, M. N. Vargaftik, I. I. Moiseev, *Russ. Chem. Bull., Int. Ed.* **2004**, 53(6), 1194.
- 68 U. R. Pillai, E. Sahle-Demessie, *J. Mol. Catal. A: Chem.* **2004**, 222, 153.
- 69 J. Alvarez, J. Liu, E. Román, A. E. Kaifer, *Chem. Commun.* **2000**, 1151.
- 70 J. Liu, J. Alvarez, W. Ong, E. Román, A. E. Kaifer, *Langmuir* **2001**, 17, 6762.
- 71 T. Ueno, M. Suzuki, T. Goto, T. Matsumoto, K. Nagayama, Y. Watanabe, *Angew. Chem. Int. Ed.* **2004**, 43, 2527.
- 72 J. Dupont, G. S. Fonseca, A. P. Umpierre, P. F. P. Fichtner, S. R. Teixeira, *J. Am. Chem. Soc.* **2002**, 124, 4228.
- 73 C. W. Scheeren, G. Machado, J. Dupont, P. F. P. Fichtner, S. R. Teixeira, *Inorg. Chem.* **2003**, 42, 4738.
- 74 E. T. Silveira, A. P. Umpierre, L. M. Rossi, G. Machado, J. Morais, G. V. Soares, I. J. R. Baumvol, S. R. Teixeira, P. F. P. Fichtner, J. Dupont, *Chem. Eur. J.* **2004**, 10, 3734.
- 75 J. Huang, T. Jiang, B. Han, H. Gao, Y. Chang, G. Zhao, W. Wu, *Chem. Commun.* **2003**, 1654.
- 76 X.-D. Mu, D. G. Evans, Y. Kou, *Catal. Lett.* **2004**, 97(3-4), 151.
- 77 J. Le Bras, D. K. Mukherjee, S. González, M. Tristany, B. Ganchegui, M. Moreno-Maas, R. Pleixats, F. Hémin, J. Muzart, *New J. Chem.* **2004**, 28, 1550.
- 78 H. Ohde, C. M. Wai, H. Kim, J. Kim, M. Ohde, *J. Am. Chem. Soc.* **2002**, 124, 4540.
- 79 B. Yoon, H. Kim, C. M. Wai, *Chem. Commun.* **2003**, 9, 1040.
- 80 H. Lindlar, *Helv. Chim. Acta* **1952**, 35, 446.
- 81 M. Bartok, J. Czombos, K. Felfoldi, L. Gera, G. Göndös, A. Molnar, F. Notheisz, I. Palinko, G. Wittmann, A. G. Zsigmond, *Stereochemistry of Heterogeneous Metal Catalysis*. John Wiley & Sons, New York, **1985**.
- 82 S. Bailey, F. King, in: R. A. Sheldon, H. van Bekkum (Eds.), *Fine Chemicals through Heterogeneous Catalysis*. Wiley, New York, **2001**, p. 351.
- 83 For recent examples, see A. Mastalir, Z. Kiraly, *J. Catal.* **2003**, 220, 372.
- 84 A. Mastalir, Z. Kiraly, Gy. Szöllosi, M. Bartok, *Appl. Catal. A* **2001**, 213, 133.
- 85 C. Lange, D. De Caro, A. Gamez, S. Stork, J. S. Bradley, W. F. Maier, *Langmuir* **1999**, 15, 5333.
- 86 H. Bönemann, W. Brijoux, K. Siepen, J. Hormes, R. Franke, J. Pollmann, J. Rothe, *Appl. Organomet. Chem.* **1997**, 11, 783.
- 87 L. M. Bronstein, D. M. Chernyshov, I. O. Volkov, M. G. Ezernitskaya, P. M. Valetsky, V. G. Matveeva, E. M. Sulman, *J. Catal.* **2000**, 196, 302.
- 88 E. Sulman, V. Matveeva, A. Usanov, Y. Kosivtov, G. Demidenko, L. Bronstein, D. Chernyshov, P. Valetsky, *J. Mol. Catal. A: Chem.* **1999**, 146, 265.
- 89 M. M. Telkar, C. V. Rode, R. V. Chaudhari, S. S. Joshi, A. M. Nalawade, *Appl. Catal. A* **2004**, 273, 11.
- 90 J. L. Pellagatta, C. Blandy, V. Collière, R. Choukroun, B. Chaudret, P. Cheng, K. Philippot, *J. Mol. Catal. A: Chem.*, **2002**, 178, 55.
- 91 H. G. Niessen, A. Eichhorn, K. Woelk, J. Bargon, *J. Mol. Catal. A: Chem.* **2002**, 182-183, 463.
- 92 K. Weissermel, H. J. Arpe, *Industrial Organic Chemistry*, 2nd edn. VCH, New York, **1993**, p. 343.
- 93 J. A. Moulijn, P. W. N. M. van Leeuwen, R. A. van Santen (Eds.), *An Integrated Approach to Homogeneous, Heterogeneous and Industrial Catalysis*. Elsevier, Amsterdam, **1995**.
- 94 A. Roucoux, Stabilized noble metal nanoparticles: An unavoidable family of catalysts for arene derivatives hydrogenation, in: C. Copéret, B. Chaudret (Eds.), *Topics in Organometallic Chemistry*. Springer, **2005**, Vol. 16, p. 261.
- 95 J. A. Widegren, R. G. Finke, *J. Mol. Catal. A: Chemical* **2003**, 187, 207.
- 96 K. R. Januszkiewicz, H. Alper, *Organometallics* **1983**, 2, 1055.
- 97 K. R. Januszkiewicz, H. Alper, *Can. J. Chem.* **1984**, 62, 1031.
- 98 K. Nasar, F. Fache, M. Lemaire, J. C. Beziat, M. Besson, P. Gallezot, *J. Mol. Catal.* **1993**, 78, 257.
- 99 T. Q. Hu, B. R. James, S. J. Rettig, C. L. Lee, *Can. J. Chem.* **1997**, 75, 1234.
- 100 T. Q. Hu, B. R. James, S. J. Rettig, C. L. Lee, *J. Pulp. Pap. Sci.* **1997**, 23, 153.

- 101 B. R. James, Y. Wang, C. S. Alexander, T. Q. Hu, *Chem. Ind.* **1998**, 75, 233.
- 102 V. Mévellec, A. Roucoux, E. Ramirez, K. Philippot, B. Chaudret, *Adv. Synth. Catal.* **2004**, 346, 72.
- 103 R. W. Albach, M. Jautelat, German Patent DE 19807995, Bayer AG **1999**.
- 104 T. Q. Hu, B. R. James, C. L. Lee, *J. Pulp. Pap. Sci.* **1997**, 23, 200.
- 105 G. S. Fonseca, A. P. Umpierre, P. F. P. Fichtner, S. R. Teixeira, J. Dupont, *Chem. Eur. J.* **2003**, 9, 3263.
- 106 G. S. Fonseca, E. T. Silveira, M. A. Gellesky, J. Dupont, *Adv. Synth. Catal.* **2005**, 347, 847.
- 107 X. D. Mu, J. Q. Meng, Z. C. Li, Y. Kou, *J. Am. Chem. Soc.* **2005**, 27, 127.
- 108 R. G. Finke, in: D. L. Feldheim, C. A. Foss, Jr. (Eds.), *Metal Nanoparticles: Synthesis, Characterization and Applications*. Marcel Dekker, New York, **2002**, Chapter 2, pp. 17.
- 109 R. J. Bonilla, P. G. Jessop, B. R. James, *Chem. Commun.* **2000**, 941.
- 110 H. Nagahara, M. Ono, M. Konishi, Fukuoka, *Appl. Surf. Sci.* **1997**, 121/122, 448.
- 111 W. Yu, Y. Wang, H. Liu, W. Zheng, *J. Mol. Catal. A: Chemical* **1996**, 112, 105.
- 112 W. Yu, M. Liu, H. Liu, X. Ma, Z. Liu, *J. Colloid Interface Sci.* **1998**, 238, 439.
- 113 H. D. Ding, D. L. Gin, *Chem. Mater.* **2000**, 12, 22.
- 114 A. Spitaleri, P. Pertici, N. Scalera, G. Vitulli, M. Hoang, T. W. Turney, M. Gleria, *Inorg. Chim. Acta* **2003**, 61.
- 115 G. S. Fonseca, A. P. Umpierre, P. F. P. Fichtner, S. R. Teixeira, J. Dupont, *Chem. Eur.* **2003**, 9, 3263.
- 116 G. S. Fonseca, J. D. Scholten, J. Dupont, *Synlett* **2004**, 9, 1525.
- 117 Y. Izumi, *Adv. Catal.* **1983**, 32, 215.
- 118 Y. Orito, S. Imai, S. Niwa, G.-H. Nguyen, *J. Synth. Org. Chem. Jpn.* **1979**, 37, 173.
- 119 Y. Orito, S. Imai, S. Niwa, *J. Chem. Soc. Jpn.* **1979**, 1118.
- 120 Y. Orito, S. Imai, S. Niwa, *J. Chem. Soc. Jpn.* **1980**, 670.
- 121 S. Niwa, S. Imai, Y. Orito, *J. Chem. Soc. Jpn.* **1982**, 137.
- 122 A. Baiker, in: D. E. De Vos, I. F. J. Vankelecom, P. A. Jacobs (Eds.), *Chiral Catalyst Immobilization and Recycling*. Wiley-VCH, Weinheim, **2000**, pp. 155.
- 123 P. B. Wells, R. P. K. Wells, in: D. E. De Vos, I. F. J. Vankelecom, P. A. Jacobs (Eds.), *Chiral Catalyst Immobilization and Recycling*. Wiley-VCH, Weinheim, **2000**, pp. 123.
- 124 M. Studer, H.-U. Blaser, C. Exner, *Adv. Synth. Catal.* **2003**, 345, 45 and references cited therein.
- 125 P. B. Wells, K. E. Simons, J. A. Slipszenko, S. P. Griffiths, D. F. Ewing, *J. Mol. Catal.* **1999**, 146, 159.
- 126 H. U. Blaser, H. P. Jallet, *J. Mol. Catal.* **1991**, 68, 215.
- 127 X. Zuo, H. Liu, M. Liu, *Tetrahedron Lett.* **1998**, 39, 1941.
- 128 B. Torok, K. Felfoldi, G. Szakonyi, K. Balazsik, M. Bartok, *Catal. Lett.* **1998**, 52, 81.
- 129 H. Bönemann, G. A. Braun, *Angew. Chem. Int. Ed. Engl.* **1996**, 35, 1992.
- 130 H. Bönemann, G. A. Braun, *Chem. Eur. J.* **1997**, 3, 1200.
- 131 J. U. Köhler, J. S. Bradley, *Catal. Lett.* **1997**, 45, 203.
- 132 J. U. Köhler, J. S. Bradley, *Langmuir* **1998**, 14, 2730.
- 133 Y. Huang, J. Chen, H. Chen, R. Li, Y. Li, L. Min, X. Li, *J. Mol. Catal.* **2001**, 170, 143.
- 134 X. Zuo, H. Liu, C. Yue, *J. Mol. Catal.* **1999**, 147, 63.
- 135 X. Zuo, H. Liu, D. Guo, X. Yang, *Tetrahedron* **1999**, 55, 7787.
- 136 X. Zuo, H. Liu, J. Tian, *J. Mol. Catal.* **2000**, 157, 217.
- 137 J. Zhang, X. Yan, H. Liu, *J. Mol. Catal.* **2001**, 175, 125.
- 138 P. J. Collier, J. A. Iggo, R. Whyman, *J. Mol. Catal.* **1999**, 146, 149.
- 139 V. Mévellec, C. Mattioda, J. Schulz, J. P. Rolland, A. Roucoux, *J. Catal.* **2004**, 225, 1.