APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 8, 361–378 (1994)

Preparation and Catalytic Properties of NR_4^+-Stabilized Palladium Colloids*

Helmut Bönnemann,† Rainer Brinkmann and Peter Neiteler‡
Max-Planck-Institut für Kohlenforschung, P.O. Box 10 13 53, D-45466 Mülheim, Germany

Palladium colloids revealing narrow particle size distributions can be obtained by chemical reduction using tetra-alkylammonium hydrotriorganoborates. Combining the stabilizing agent [NR_4^+] with the reducing agent [BEt_3H^-] provides a high concentration of the protecting group at the reduction centre. Alternatively, NR_4X (X = halogen) may be coupled to the metal salt prior to the reduction step: addition of $N(octyl)_4Br$ to $Pd(ac)_2$ in THF, for example, evokes an active interaction between the stabilizing agent and the metal salt. Reduction of NR_4^+-stabilized palladium salts with simple reducing agents such as hydrogen at room temperature yields stable palladium organosols which may be isolated in the form of redispersible powders. The anion of the palladium salt is crucial for the success of the colloid synthesis. Electron microscopy shows that the mean particle size ranges between 1.8 and 4.0 nm. An X-ray-photoelectron spectroscopic examination demonstrated the presence of zerovalent palladium.

These palladium colloids may serve as both homogeneous and heterogeneous hydrogenation catalysts. Adsorption of the colloids onto industrially important supports can be achieved without agglomeration of palladium particles. The standard activity of a charcoal catalyst containing 5% of colloidal palladium determined through the cinnamic acid standard test was found to exceed considerably the activity of the conventional technical catalysts. In addition, the lifespan of the catalyst containing a palladium colloid, isolated from the reduction of $[N(octyl)_4]_2PdCl_2Br_2$ with hydrogen, is superior to conventionally prepared palladium/charcoal (Pd/C) catalysts. For example, the activity of a conventional Pd/C catalyst is completely suppressed after 38×10^3 catalytic cycles per Pd atom, whereas the colloidal Pd/C catalyst shows activity even after 96×10^3 catalytic cycles.

Keywords: Palladium colloids, catalysis, hydrogenation

INTRODUCTION

In applied organometallic chemistry the main field of manoevres is catalysis. In the area of homogeneous catalysis, the concept of molecular catalyst design, including the control of the most subtle ligand effects, has led to significant technological progress.[1,2] In contrast to this now relatively mature area of science, the application of metal clusters and metal colloids as molecularly designed precursors for hetereogeneous catalysts has long been neglected. This phase of hibernation was probably due to the preconception that nanometal particles of less than 10 nm diameter would be unstable, troublesome to isolate in sufficient quantities, and difficult to transfer onto supports without agglomeration. Notably, the fundamental work of Bradley,[3,4] Braunstein,[5] Gates,[6,7] Esumi,[8,9] Evans,[10–13] Heaton,[14–17] Klabunde,[18–24] Knözinger,[6,25] Lewis,[26] Moiseev,[27–33] Schmid,[34–45] and Toshima[46–55] established an essential part of a potential innovation in catalytic technology, revitalizing the 'precursor-concept' through utilizing mono- and even multi-component nanometals for the design of advanced heterogeneous catalysts. This goal, however, will only be achieved by a close, interdisciplinary collaboration of synthetic chemistry, physical analysis, and industrial chemistry. We were able to develop two general routes for the preparation of nanoscale mono- and bi-metallic colloids derived from the elements of Groups 6–11, protected by tetra-alkylammonium groups.[56–61] These materials have a narrow particle size distribution, are very stable, and may be handled at high concentrations. Furthermore, electron microscopy confirmed that

---

* Dedicated to Professor H. Werner on the occasion of his 60th anniversary in recognition of his important contributions to pure and applied organometallic chemistry.

† Author to whom correspondence should be addressed.

‡ Present address: Aral AG, Querenburger Straße 46, D-44789 Bochum, Germany.

CCC 0268–2605/94/040361–18
© 1994 by John Wiley & Sons, Ltd.

Received 23 February 1994
Accepted 4 April 1994

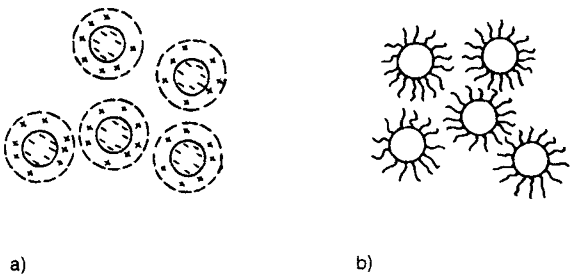


Figure 1 (a) Electrostatic and (b) steric stabilization of palladium.[63]

the discrete metal particles may be deposited onto supports without any unwanted agglomeration. So these materials fulfil all the major prerequisites necessary for precursors employed in heterogeneous catalysis.

Ilya Moiseev and Michael Vargaftik are true pioneers of catalysis involving giant palladium clusters, which contain several hundred metal atoms and combine high catalytic activity with unusual selectivity properties.[62] The goal of our work was to apply our various preparative methods[57, 58, 60, 61] towards the synthesis of NR_4^+-stabilized nanoscale palladium organosols. Furthermore, the utility of these palladium colloids as precursors for the production of novel heterogeneous hydrogenation catalysts will be elucidated, including the evaluation of these systems with respect to activity, selectivity and durability, using industrial standard quality tests.

CONCEPTS OF COLLOID STABILIZATION

Metal colloids, in contrast to clusters, do not represent chemical compounds having well-defined metal–metal bonds of known nuclearity, but consist of a mixture of nanocrystalline metal particles, which can be redispersed in solvents, characterized by their particle size distribution. In general, the diameter of zerovalent metal colloids found by electron microscopy ranges between 1 and 15 nm. For catalytic applications, a narrow particle size distribution is essential. Agglomeration of the metal particles to give non-redispersible precipitates may be prevented either through electrostatic charge repulsion (Fig. 1a) or by covering the metal cores using appropriate protecting molecules (Fig. 1b).

The stabilization concept of the type (a) is based on the assumption of the formation of electrochemical double layers at the particle surface, and is especially effective in solvents having high dielectricity constants, such as water. Electrostatic particle stabilization has been rationalized by the Derjaguin–Landau–Verwey–Overbeek theory[63] and was convincingly verified by the excellent work of Turkevich.[64, 65] Using the stabilization concept of type (b), the agglomeration of nanometal particles is prevented through an outer protective shell. Van der Waals repulsion, e.g. of long-chain alkyl substituents in the shielding molecules bonded to the particle surface, results in a considerable stabilization effect via a conformational reduction of entropy (Fig. 2).

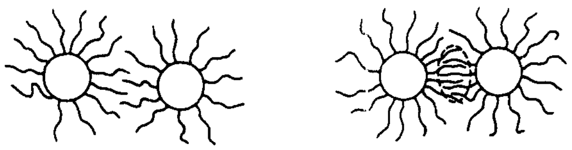


Figure 2 Conformational entropy reduction of the alkyl chain upon the approach of two particles.[63]

Cationic tensides such as tetra-alkylammonium halides have been used as highly functional protecting groups for nanometals.[66–68] The bonding between the physisorbed NR_4^+ moiety and a silver surface (Fig. 3) has been demonstrated by Wiesner *et al.*[68] via surface-enhanced Raman spectroscopy (SERS).

Esumi and co-workers[66] first applied the method of solvent–solvent extraction for the phase-transfer of insoluble palladium chloride ($PdCl_2$) and platinum chloride ($PtCl_2$) from water into organic media, e.g. chloroform or isobutyl methyl ketone using distearyldimethylammonium chloride or trioctylmethylammonium chloride. The subsequent reduction of the extracts in the organic phase with, for example, formaldehyde, hydrazine, hydrogen or sodium borohydride ($NaBH_4$) led to colloidal metals stabilized by NR_4X (Fig. 4). We were able to show that the

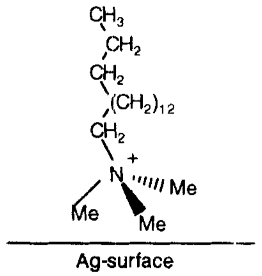
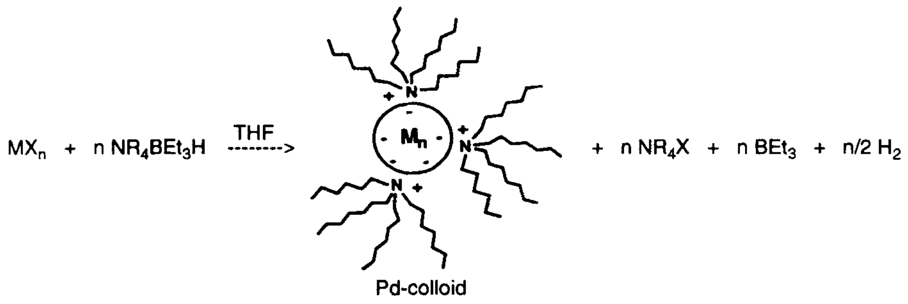


Figure 3 Interaction between N(cetyl)(Me)$_3$Br and the silver surface.[69]



M = metals of the groups 6 - 11; X = Cl, Br; n = 2, 3; R = Alkyl, C_4 - C_{20}

Figure 4 Formation of NR_4^+-stabilized metal colloids employing a combined stabilizing/reducing agent.

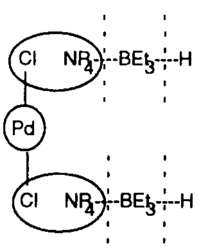


Figure 5 Schematic representation of the reducing process.

combination of the stabilizing agent NR_4^+ with the reducing agent BEt_3H^- opens a direct access in organic media to stable and highly concentrated metal colloids having narrow size distributions.[57,59–61] The advantage of this method, which we have successfully utilized for the preparation of colloidal mono- and polymetals of Groups 6–11, resides in an entropic stabilization factor, in other words, a high concentration of the stabilizing agent can be built up directly at the reduction centre (Fig. 5).

The restriction to one special type of reducing agent, together with the compulsory requirement of stoichiometric amounts of the stabilizing agent, led us to the idea of coupling the stabilizing NR_4^+ to the metal salt prior to reduction, which can now be performed using simple inorganic or organic reductants[58] (Eqn [1]).

$$(NR_4)_mMX_nY_m + n\ \mathrm{Red} \rightarrow M_{\mathrm{coll.}} + n\ \mathrm{RedX} + m\,NR_4Y \qquad [1]$$

M = Groups 6–11 element
Red = H_2, HCOOH, BEt_3, K, Zn, LiH, $LiBEt_3H$, $NaBEt_3H$, $KBEt_3H$
X, Y = Cl, Br, I

$n, m = 1$–3
$R = C_4$–C_{12}

The stabilizing agent [e.g. $N(octyl)_4Br$] can also be connected to the metal as a tetra-alkylammonium metallate (Eqn [2]).

$$PdX_2 + 2N(\mathrm{octyl})_4Y \xrightarrow[\mathrm{THF}]{16\ \mathrm{h,\ reflux}} [N(\mathrm{octyl})_4]_2PdX_2Y_2 \qquad [2]$$

X, Y = Cl, Br

Insoluble palladium halides can be transformed into alkylammonium palladates, which are very soluble in organic phases, simply by suspending in tetrahydrofuran (THF) in the presence of NR_4^+X and slowly warming up. Both of our preparative methods, which lead to stable nanometal colloids with narrow particle size distributions, are represented in Fig. 4 and Eqn. [1]. The resulting colloids can be easily isolated and handled in various solvents at unusually high metal concentrations.

EXPERIMENTAL

All experiments were carried out strictly under argon (NmL = mL gas under normal conditions).

Preparation of tetra-alkylammonium triethylhydroborates

The coupling of the NR_4^+ group with the reducing hydrides was achieved by following the general procedure given previously, viz. in Refs 56, 60 and 61.

$N(dodecyl)_2(Me)_2[BEt_3H]$

A 0.156 M solution (20 ml; 31.20 mmol) of $K[BEt_3H]$ in THF was added dropwise and with

stirring at 20 °C to 14.44 g (31.2 mmol) of N(dodecyl)$_2$(Me)$_2$Br in 40 ml of THF. After heating at 55 °C for 1 min, the reaction mixture was stirred for an additional 8 h at 0 °C; the white potassium bromide (KBr) precipitate was filtered off at 0 °C and washed three times with 20 ml of THF. The hydride content of the clear solution was determined (volumetrically) by hydrolysis with 1 N HCl.
Content: 0.216 mol l^{-1} Yield: 130 ml (90%). ^{11}B NMR spectra (−30 °C): $\delta = 57.8$ (d, $J_{BH} = 64.6$ Hz). Potassium content of the solution: 0.26 mg per 10 ml. Gas evolved during thermal decomposition (3 h, 60 °C): 48.8 Nml CH$_4$ per 10 ml solution.

N(dodecyl)$_4$[BEt$_3$H]

A 0.156 M solution (20 ml; 15.6 mmol) of K[BEt$_3$H] in THF was added dropwise and with stirring at 20 °C to 12.04 g (15.6 mmol) of N(dodecyl)$_4$Br in 50 ml of THF. After being heated for 1 min at 60 °C the reaction mixture was filtered and the white precipitate washed three times with 10 ml of THF. The hydride content of the clear solution was measured volumetrically by hydrolysis with 1 M HCl. Content: 0.148 mol l^{-1}. Yield: 100 ml (95%). ^{11}B NMR spectra: $\delta = 11.8$ (s). Potassium content of the solution: 0.03 mg per 10 ml. No gas evolved during thermal decomposition (3 h, 60 °C).

N(benzyl)(dodecyl)(Me)$_2$[BEt$_3$H]

A 0.156 M solution (9.7 ml; 30.75 mmol) of K[BEt$_3$H] in THF was added dropwise and with stirring at 20 °C to 11.82 g (30.75 mmol) of N(benzyl)(dodecyl)(Me)$_2$Br in 40 ml of THF. After being stirred at 20 °C for 90 min, the reaction mixture was filtered at −20 °C and the precipitate washed three times with 20 ml of THF. The hydride content of the clear solution was measured by hydrolysis with 1 M HCl. Content: 0.19 mol l^{-1}. Yield: 130 ml (80%). ^{11}B NMR spectra (−30 °C): $\delta = 57$ (s). Potassium content of the solution: 0.06 mg per 10 ml. Gas evolved during thermal decomposition (3 h, 60 °C): 16.8 Nml/10 ml solution.

Preparation of [Pd(CO)(ac)]$_4$ · acH

Palladium acetate [Pd(ac)$_2$] (3.95 g; 17.6 mmol) was stirred in 400 ml of acetic acid for 16 h under a pressure of 1 bar CO. The resulting light-yellow precipitate was filtered off and washed with 10 ml of acetic acid. Drying under vacuum yielded 2.84 g (72%) [Pd(CO)(ac)]$_4$ · acH (where ac = acetate). Elemental analysis: Pd, 47.80; C, 21.61; H, 2.21%. MS: *m/z* 28 [CO$^+$], 60 [CH$_3$COOH$^+$], 452 [Pd$_2$ · 2 CH$_3$COOH · 2 CH$_3$COO$^+$].

Preparation of NR$_4^+$-palladates

[N(octyl)$_4$]$_2$PdCl$_2$Br$_2$

A quantity of 0.25 g (1.41 mmol) of PdCl$_2$ was heated to reflux for 16 h in a solution of 1.56 g (2.85 mmol) of N(octyl)$_4$Br in 30 ml of THF. The PdCl$_2$ dissolved and a deep-red solution emerged. This solution was diluted with THF to a palladium concentration of 0.02 mol l^{-1}. For an elemental analysis, an aliquot of the suspension was evaporated and dried under vacuum for 3 h. Elemental analysis: Pd, 7.74; Cl, 5.64; Br, 11.27; C, 60.54; H, 10.59; N, 2.92%. [N(octyl)$_4$]$_2$PdCl$_2$Br$_2$ can also be prepared from PdBr$_2$ or N(octyl)$_4$Cl.

[N(octyl)$_4$]$_2$PdCl$_4$ and [N(octyl)$_4$]$_2$PdBr$_4$

The preparation of [N(octyl)$_4$]$_2$PdCl$_4$ and [N(octyl)$_4$]$_2$PdBr$_4$ was the same as that for [N(octyl)$_4$]$_2$PdCl$_2$Br$_2$, employing the appropriate combination of starting materials.

Preparation of NR$_4^+$-protected palladium colloids

Reduction with NR$_4^+$BR$_3$H

PdCl$_2$/N(octyl)$_4$BEt$_3$H (colloid C01) To a suspension of palladium chloride (PdCl$_2$) (3.52 g; 19.8 mmol) in THF (500 ml), a solution of N(octyl)$_4$BEt$_3$H in THF (0.397 M; 100 ml) was added at 23 °C in 1 h. The PdCl$_2$ dissolved completely within 3 h at 23 °C. After 16 h a dark-brown solution was formed and the volatile compounds were removed through evaporation. The dark-brown, waxy residue was dried at 40 °C and 10^{-3} mbar for 3 h. The product (28.8 g) proved soluble in THF, ether, toluene, and acetone, but insoluble in ethanol, and contained 7.3% of palladium. Thereafter, the residue was dissolved in 640 ml of technical-quality ether without using an inert gas atmosphere. Addition of 64 ml of technical ethanol to the ether solution caused the formation of a grayish-brown precipitate. The precipitate was allowed to settle for 1 h before the clear supernatant solution was removed by applying pressure of an inert gas on the liquid surface. The precipitate was then washed with a mixture of 150 ml of ether/15 ml of ethanol. Drying under vacuum (10^{-3} mbar, 25 °C, 20 min) yielded a gray

colloidal powder (1.8 g) which proved to be very soluble in THF, soluble in acetone and insoluble in toluene or ether. Palladium content: 83.6%. Transmission electron microscopy (TEM): mean particle size, 2.5 nm.
X-ray photoelectron spectroscopy (XPS): palladium (0).

$PdCl_2/N(octyl)_4BEt_3$–H_2 after treatment (colloid C02) A solution of the colloid (**C01**) in THF was stirred for seven days at 20 °C under a hydrogen atmosphere (1.5 bar). TEM: mean particle size, 3.2 nm.

The following colloids were not purified and aliquots of the resulting reaction mixtures were supported directly on the carrier charcoal. The dissolved colloidal palladium can be converted into palladium(0) powder by hydrolysis with ethanol.

$PdCl_2/N(dodecyl)_4BEt_3H$ (colloid C03) To a suspension of $PdCl_2$ (0.177 g; 1 mmol) in THF (25 ml), a solution of $N(dodecyl)_4BEt_3H$ (2 mmol) in THF (25 ml) was added at 20 °C in 15 min and the mixture was stirred for an additional 3 h. Gas liberated: 17.0 Nml H_2 (76%). An aliquot of the solution was evaporated and dried under vacuum at 20 °C for 3 h. Elemental analysis: Pd, 10.15; Cl, 6.65; B 0.53%.

$PdCl_2/N(dodecyl)_2(Me)_2BEt_3H$ (colloid C04) To a suspension of $PdCl_2$ (0.177 g; 1 mmol) in THF (25 ml), a solution of $N(dodecyl)_2(Me)_2BEt_3H$ (2 mmol) in THF (25 ml) was added at 20 °C in 15 min and the mixture was stirred for an additional 3 h. Gas liberated: 17.0 Nml H_2 (76%). An aliquot of the solution was evaporated and dried under vacuum at 20 °C for 3 h. Elemental analysis: Pd, 10.15; Cl, 6.65; B, 0.53%.

$PdBr_2/N(octyl)_4BEt_3H$ (colloid C05) To a solution of palladium bromide ($PdBr_2$) (0.266 g; 1 mmol) in THF (25 ml), a solution of $N(octyl)_4BEt_3H$ (2 mmol) in THF (25 ml) was added at 20 °C in 15 min. Stirring for an additional 3 h produced a colloidal solution together with a palladium precipitate which was removed by filtration. Gas liberated: 15.5 Nml H_2 (69%). Palladium content of the solution: 0.67 mg ml (31.5%).

$PdI_2/N(octyl)_4BEt_3H$ (colloid C06) To a solution of palladium iodide (PdI_2) (0.36 g; 1 mmol) in THF (25 ml), a solution of $N(octyl)_4BEt_3H$ (2 mmol) in THF (25 ml) was added, while avoiding any exposure to light, at 20 °C in 15 min, and the mixture was stirred for an additional 3 h. Gas liberated: 19.0 Nml H_2 (85%). An aliquot of the solution was evaporated and dried under vacuum for 3 h at 20 °C. Elemental analysis: Pd, 6.78; I, 12.16; B, 0.0%.

$(allylPdCl)_2/N(octyl)_4BEt_3H$ (colloid C07) To a solution of $(allylPdCl)_2$ (0.183 g; 1 mmol) in THF (25 ml), a solution of $N(octyl)_4BEt_3H$ (1 mmol) in THF (25 ml) was added at 20 °C in 15 min and the mixture was stirred for an additional 3 h. Gas liberated: 3.0 Nml H_2 (78.0%). An aliquot of the solution was evaporated and dried under vacuum at 20 °C for 3 h. Elemental analysis: Pd, 16.0; Cl, 5.26; B, 1.21%.

$Pd(ac)_2/N(octyl)_4BEt_3H$ (colloid C08) To a solution of $Pd(ac)_2$ (0.225 g; 1 mmol) in THF (25 ml), a solution of $N(octyl)_4BEt_3H$ (2 mmol) in THF (25 ml) was added at 20 °C in 15 min and the mixture was stirred for an additional 3 h. Gas liberated: 13.9 Nml H_2 (62%). Again, an aliquot of the solution was evaporated and dried under vacuum at 20 °C for 3 h. Elemental analysis: Pd, 9.04; B, 0.0%.

Reduction with hydrogen

$Pd(ac)_2/N(dodecyl)_4Br/H_2$ (colloid C09) The preparation for this colloid is given previously.[59]

$[N(octyl)_4]_2PdCl_2Br_2/H_2$ (colloid C10) A solution of $[N(octyl)_4]_2PdCl_2Br_2$ (50 ml; 0.02 mol Pd l^{-1}) was stirred at 20 °C for 14 days under a hydrogen atmosphere, producing a colloidal solution of palladium. Hydrogen absorption: 25.3 Nml (113%). TEM:mean particle size, 4.0 nm.

Reduction with BEt_3

$Pd(ac)_2/N(dodecyl)_4Br/BEt_3$ (colloid C11) To a solution of $Pd(ac)_2$ (0.5 g; 2.23 mmol) and $N(dodecyl)_4Br$ (1.0 g; 1.3 mmol) in THF (52 ml), a solution of BEt_3 (0.383 mol BEt_3 l^{-1}; 58.1 ml) in THF was added at 20 °C in 15 min. The solution turned black and, over a period of eight days 99.3 Nml gas (ethane, ethene) was produced. TEM: mean particle size, 2.5 nm.

The addition of 55 ml of water (under argon) resulted in a brown–black precipitate. After the suspension had been allowed to stand for 16 h, the supernatant solution was removed under pressure and the precipitate dried under vacuum at

20 °C for 3 h. The resulting black powder (0.25 g, 75%) was soluble in THF and contained 71.3 wt% palladium.

Reduction with formic acid (HCOOH)

Pd(ac)$_2$/N(dodecyl)$_4$Br/HCOOH (colloid C12) A THF solution (90 ml) containing Pd(ac)$_2$ (0.4 g; 1.78 mmol), N(dodecyl)$_4$Br (0.8 g; 1.04 mmol) and HCOOH (0.8 g; 17.4 mmol) were heated at 60 °C for 16 h. The solution turned black and 68.4 Nml gas (CO, CO$_2$) was generated in 16 h. TEM: mean particle size, 1.8 nm. The addition of 50 ml of water (under argon) resulted in a brown–black precipitate. After the suspension had been allowed to stand for 16 h, the supernatant solution was removed by applying pressure and the precipitate was dried under vacuum at 20 °C for 3 h. The resulting black powder (0.21 g; 81%) proved to be soluble in THF and contained 73.44 wt% palladium.

Thermolysis of Pd(ac)$_2$ in the presence of N(dodecyl)$_4$Br at 125 °C

Pd(ac)$_2$/N(dodecyl)$_4$Br/125 °C (colloid C13) A mixture of Pd(ac)$_2$ (0.4 g; 1.7 mmol) and N(dodecyl)$_4$Br (0.8 g; 1.03 mmol) in *p*-xylene (90 ml) was heated at 125 °C for 3 h, producing a black solution. Gas liberated: 5.6 Nml CO$_2$. The solvent was removed through evaporation and the residue dissolved in 90 ml of THF. TEM: mean particle size, 2.1 nm. The addition of a mixture of 180 ml ethanol/15 ml water resulted in a brown–black precipitate. After the suspension had been allowed to stand for 16 h, the supernatant solution was removed by applying pressure and the precipitate dried under vacuum at 20 °C for 3 h. The resulting black powder (0.21 g; 96%) was soluble in THF and contained 86.3 wt% palladium.

Preparation of a supported palladium catalyst and initial hydrogenation activity in the cinnamic acid standard test

For all catalysis testing, the active charcoal support utilized was supplied by Degussa (material 101, charge 514). The support was produced using charcoal generated from wood and showed the physical properties summarized in Table 1.

General procedure

To a suspension of approximately 1.0 g of charcoal (weighed to a precision of 0.001 g) in 30 ml of THF, a THF solution containing palladium colloid was added with stirring at 20 °C. Sufficient palladium colloid was added to achieve 5 wt% of palladium with respect to the dried mass. After stirring for 16 h, the suspension was filtered off and the precipitate washed three times with 10 ml of THF. After it had been dried under vacuum for 16 h, the catalyst was oxidized in air for 16 h at pressure of 1 mbar. THF content (mean value): 17 wt% in the non-oxidized catalyst and 15 wt% in the oxidized catalyst. The charcoal-supported palladium colloids are pyrophoric.

Details of the preparation procedure for the individual catalysts are shown in Table 2.

For the performance of the cinnamic acid standard test and the apparatus used, see Ref. 59, pp. 162 and 173.

Standard testing procedure for the lifespan of the catalysts

The lifespan of a supported palladium catalyst was determined by measuring the catalytic hydrogenation of a test substrate, cyclo-octene, employing a hydrogenation apparatus operating in semicontinuous mode as described in Ref. 59. Under an inert atmosphere, *ca* 150 mg of palladium catalyst was weighed, with an accuracy of 0.1 mg, into a 100 ml dropping funnel. The dropping funnel was then connected to the experimental setup and the entire apparatus was completely evacuated and backfilled with hydrogen several times. The catalyst, together with 90 ml cyclo-octene, was transferred to the reactor. The dropping funnel was flushed with 30 ml ethanol. The catalyst suspension was equilibrated at 40 °C. Subsequently, the line to the hydrogen supply (0.2 l; 100 bar) was opened and the pressure was adjusted by a pressure-reducing valve to 1 bar. At the same time, the stirrer in the reactor was put into operation. The uptake of hydrogen was registered on a chart recorder as pressure drop in the

Table 1 Physical properties of active charcoal support

Bulk density (g ml)	approx. 0.4
Average grain size (μm)	25
BET specific surface area[a] (m^2 g^{-1})	993
Pore volume (ml g^{-1})[b]	
Total	1.01
Micropores ($r < 1$ nm)	0.35
Mesopores (1 nm $< r <$ 15 nm)	0.35
Macropores (15 nm $< r <$ 100 nm)	0.31

[a] Determined by nitrogen sorption. [b] Mercury penetration.

Table 2 Catalyst preparation

Catalyst no.	Precursor	Supporting procedure
1	$PdCl_2/N(octyl)_4BEt_3H$ (**C01**)	Analogous to the general procedure.
2	$Pd(ac)_2/N(dodecyl)_4Br$/125 °C (**C13**)	Analogous to the general procedure.
3	$[N(octyl)_4]_2PdCl_2Br_2/H_2$ (**C10**)	Analogous to the general procedure.
4	$Pd(ac)_2/N(dodecyl)_4Br$/125 °C (**C13**)	The colloid was stirred for 16 h at 20 °C under an H_2 atmosphere (1 bar) before fixing onto the support according to the general procedure.
5	$PdCl_2/N(octyl)_4BEt_3H$ (**C01**)	The general procedure was carried out under an H_2 atnmosphere (1 bar).
6	$PdCl_2/N(octyl)_4BEt_3H$ (**C02**) (H_2 after-treatment)	Analogous to the general procedure.
7	$PdCl_2/N(octyl)_4BEt_3H$ (**C01**)	The charcoal was doped with bis(toluene)titanium[57] (0.2% Ti/C) before fixing the colloid onto support according to the general procedure.
8	$PdCl_2/N(octyl)_4BEt_3H$ (**C01**)	The charcoal was doped with Ti × 0.5 THF[59, 64] (0.2%Ti/C) according to Ref. 57 before supporting the colloid analogously to the general procedure.
9	$Pd.Cl_2/N(octyl)_4BEt_3H$ (**C01**)	The charcoal was doped with a solution of a reduced titanium system (0.2%Ti/C) prepared from Ti_4 and $N(octyl)_4BEt_3H$ before fixing the colloid onto the support according to the general procedure.
10	$PdCl_2/N(octyl)_4BEt_3H$ (**C01**)	The charcoal was doped with a solution of $TiCl_3$ (0.1%Ti/C) in 0.1 M HCl and dried under vacuum for 3 h at 60 °C before fixing the colloid onto the support according to the general procedure.
11	$PdCl_2/N(octyl)_4BEt_3H$ (**C01**)	The charcoal was treated with 0.1 M HCl and dried for 3 h at 60 °C under vacuum before fixing the colloid onto the support according to the general procedure.

autoclave. When no further pressure drop was noted, the hydrogen feed was interrupted and the apparatus was flushed with argon. The suspension was then siphoned into a centrifuge tube and centrifuged for 1 h at 2000 rpm (still working under argon). The supernatant was then siphoned off and analyzed by GC to contain 99.8% cyclo-octane. The catalyst was resuspended in 90 ml cyclo-octene and again loaded into the hydrogenation reactor. The apparatus was rinsed with 30 ml ethanol. After it had been flushed with hydrogen, the lifespan experiment was continued as described above. During the first 120 min, the activity was determined as in Ref. 59; the TON was calculated for each hydrogenation cycle using the recorded pressure drop, which was taken to correspond to 100% conversion. When the measured activity at the beginning of a run fell below the minimum value of 30 $Nml\,g^{-1}\,min^{-1}$, the lifespan experiment was deemed complete.

Standard testing procedure for the selectivity of the catalysts in the hydrogenation of 1,5-cyclo-octene

The selectivity of a palladium catalyst was determined using an apparatus described previously,[59] appropriate for measuring catalytic activity. A 150 mg portion of catalyst was weighed, to an accuracy of 0.1 mg, into a 100 ml dropping funnel. The dropping funnel was then connected to the reactor and the complete apparatus was evacuated and backfilled with hydrogen several times. Subsequently the catalyst in the dropping funnel, together with 100 ml ethanol, was transferred into the reactor. The reactor was continuously flushed with hydrogen. The dropping funnel was disconnected and replaced with a septum, through which 10 ml of 1,5-cyclo-octadiene was injected into the reactor. Once the suspension was equilibrated to 25 °C and a pressure equilibrium was achieved, the apparatus was linked to a mercury-sealed 1 l precision gas burette filled with hydrogen. After a gas uptake of 700 Nml, the first 0.5 ml GC sample was pulled off through a syringe equipped with a steel cannula and a filter. At equal time intervals, six additional GC samples were taken. The selectivity of the catalyst during the hydrogenation of 1,5-cyclo-octadiene to cyclo-octene was determined as follows. The concentration of cyclo-octene was allowed to pass through a maximum. The course of the curve for percentage of cyclo-octene was approximated near the maximum with a parabolic curve, and the highest percentage content was computed mathematically. The selectivity of the catalysts and colloids in THF was determined in a similar manner.

RESULTS AND DISCUSSION

NR_4^+-protected palladium colloids via reduction of palladium salts with NR_4BEt_3H

Prior to the colloid synthesis according to Fig. 4, the protecting group NR_4^+ is coupled with the reducing agent BR_3H^- in a metathesis step (Eqn [3]).

$$KBEt_3H + NR_4Br \xrightarrow{THF} NR_4BEt_3H + KBr \qquad [3]$$

$R = \text{alkyl}\ C_1–C_{12}$

The byproduct potassium bromide forms as a very fine precipitation in THF; to assure completion of the precipitation process, it is advisable to allow the reaction mixture to stand for a few days at 0 to −5 °C before filtering potassium bromide from the solution containing the alkylammonium borate. For a successful synthesis of the colloids, the NR_4-borate solutions must be completely free of potassium. In order to achieve quantitative conversion of $KBEt_3H$, a small excess of NR_4X is used and the reaction mixture is heated to 50–60 °C for 1–2 min. Whereas the $N(octyl)_4$ and $N(dodecyl)_4$ borates are thermally quite stable, other derivatives, namely the benzyl compounds, tend to decompose according to Eqn [4] and are therefore stored at −30 °C.

$$N(R^1)_3R^2BEt_3H \xrightarrow[\Delta]{THF} N(R^1)_2R^2 + BEt_3 + CH_4 \qquad [4]$$

$R^1 = CH_3$
$R^2 = \text{dodecyl, octadecyl}$

The small quantities of amine formed during the decomposition of the reducing agent do not affect the success of the colloid preparation. The reduction of the THF-suspended palladium halides by 0.02 M borate solutions at room temperature according to Eqn [5] yields 'raw' NR_4^+–palladium colloids in the form of dark solutions.

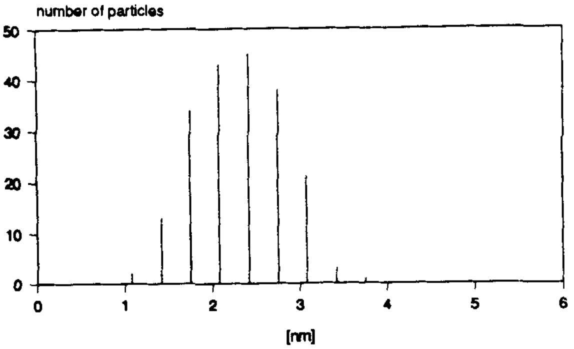
$$PdX_2(s) + 2N(octyl)_4BEt_3H \xrightarrow{THF} Pd_{coll} + 2N(octyl)_4X + 2\,BEt_3 + H_2 \qquad [5]$$

$X = Cl, Br, I$

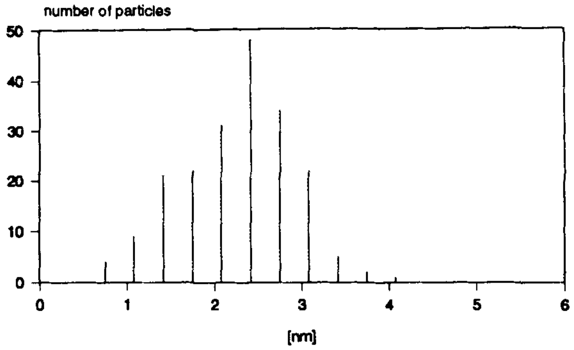
$PdCl_2$ is transformed into a metal colloid according to Eqn [5] with over 80% yield. The initial dissolved colloid can be purified by completely evaporating the THF off under high vacuum, redissolving the waxy residue in ether, and then precipitating metal colloid through addition of ethanol. The resulting, purified, grey–black palladium-colloid powders have a metal content of >80%. The processed product is fully redispersible in various organic solvents (e.g. ethers, hydrocarbons, esters, etc.) up to 1 mol l^{-1} of metal. The mean particle diameter of the resulting NR_4^+-stabilized palladium colloid according to TEM is 2.5 nm. In an XPS study of the palladium colloid, the binding energy for the Pd $3d_{5/2}$ level was found to be 334.3 eV and for the Pd $3d_{3/2}$ level, 339.9 eV. These values are comparable with those expected for Pd(0) (334.9 eV and 340.1 eV respectively). The anion selection is important. The best results were obtained using either the chloride or acetate as starting materials, whereas the bromide and iodide led to considerable amounts of black Pd(0) precipitate. Through the reduction of $[PdCl(C_3H_5)]_2$ using one equivalent of $N(octyl)_4BEt_3H$ in THF solution, a palladium colloid is also accessible. Slight variation in the particle size distribution is observed for the palladium colloids resulting from different starting materials (Eqn [5]). The particle size distributions (based on the examination of 200 particles in the TEM photographs) are compared in Fig. 6. The palladium colloid prepared from $PdCl_2$ shows the narrowest size distribution in this series.

NR_4^+-protected palladium colloids via reduction of NR_4^+ palladates using conventional reducing agents

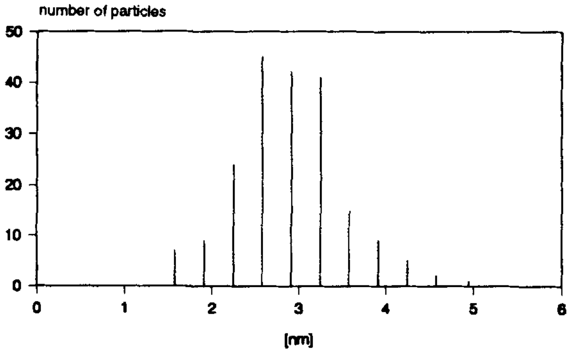
Refluxing palladium halides according to Eqn [2] with NR_4^+ halides in THF yields the corresponding NR_4^+ palladates in concentrated THF solution; these soluble intermediates are excellent starting materials for the reductive synthesis of NR_4^+-stabilized palladium colloids with conventional reducing agents such as hydrogen (see Eqn [1]). Again, the choice of the appropriate anion is crucial: the reduction of $N(octyl_4)_2PdCl_4$ with hydrogen generates only metallic precipitate and $N(octyl_4)_2PdBr_4$ cannot be reduced, even under 50 bar hydrogen atmosphere. $N(octyl_4)PdCl_2Br_2$, however, is slowly reduced by hydrogen, yielding a palladium colloid showing a mean particle dia-



colloid C01



colloid C07



colloid C08

Figure 6 Particle size distribution of the palladium colloids **C01** (see Table 3), **C07** and **C08**.

meter of 4 nm and a narrow particle size distribution (see Fig. 7 and Table 3, **C10**).

The stabilizing agent may also be combined with the metal salts in a non-stoichiometric ratio. On the addition of N(octyl)$_4$Br or N(dodecyl)$_4$Br to a solution of Pd(ac)$_2$ in THF, a strong color intensification is observed which indicates that the desired interaction between the palladium salt and the stabilizing agent has occurred. The NR$_4^+$-stabilized palladium colloids may now be obtained by simply bubbling hydrogen through the solution at room temperature. The optimal ratio of stabilizing agent to palladium is 1:2, which means that, in contrast to the synthesis shown in Fig. 4, this technique requires only about a quarter of the stabilizing agent, which considerably facilitates the workup. Reduction of Pd(ac)$_2$/N(dodecyl)$_4$Br with hydrogen leads to colloidal palladium in solution with acetic acid as the side product. The raw metal colloid is precipitated through the addition of water to give a redispersible colloid powder containing particles with a mean diameter of 1.8 nm and consisting of 77 wt% of palladium (Table 3, **C09**). The binding energy for the electron in the Pd $3d_{3/2}$ and Pd $3d_{3/2}$ level was found through XPS to be 334.5 eV and 339.9 eV respectively, which confirms that Pd(0) is present in the colloid. Colloidal Pd(0) stabilized by N(dodecyl)$_4$Br can also be obtained through reduction of NR$_4$Br/Pd(ac)$_2$ using formic acid (Table 3, **C12**) or triethylborane (Table 3, **C11**). The thermal decomposition of Pd(ac)$_2$ in *p*-xylene at 125 °C in the presence of N(dodecyl)$_4$Br also leads to the formation of colloidal Pd(0), as confirmed by TEM and XPS (Table 3, **C13**). Carbon dioxide (CO$_2$) and acetic acid were identified as the main decomposition products. The raw colloid was precipitated from the *p*-xylene by adding ethanol and small amounts of water. The purified Pd(0) colloid contains 86% of palladium and was shown to be completely redispersible in organic media. Figure 8(a–d) shows the effect of the different means of reduction on the particle size distributions (as seen in TEM) of the resulting Pd(0) colloids **C09**, **C11**, **C12** and **C13**.

The preparative results of the different routes

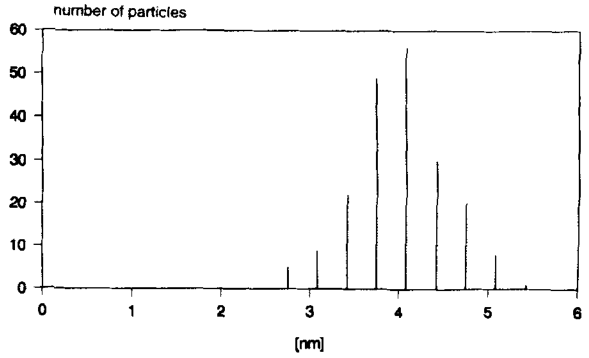


Figure 7 Particle size distribution in colloid **C10** (see Table 3).

Table 3 Preparation of NR_4^+ stabilized palladium colloids[a]

Colloid no.	Precursor	Reducing agent	Conditions t (h)	T (°C)	Solvent	Metal content in isolated colloid (%)	Mean particle size (nm)
C01	PdCl2	$N(octyl)_4BEt_3H$	1	23	THF	83	2.5
C09	$Pd(ac)_2/N(dodecyl)_4Br$	H_2	16	22	THF	77	1.8
C10	$[N(octyl)_4]_2PdCl_2Br_2$	H_2	336	22	THF	—	4.0
C11	$Pd(ac)_2/N(dodecyl)_4Br$	BEt_3	192	22	THF	71	2.5
C12	$Pd(ac)_2/N(dodecyl)_4Br$	HCOOH	16	60	THF	73	1.8
C13	$Pd(ac)_2/N(dodecyl)_4Br$	—	3	125	*P*-Xylene	86	2.1

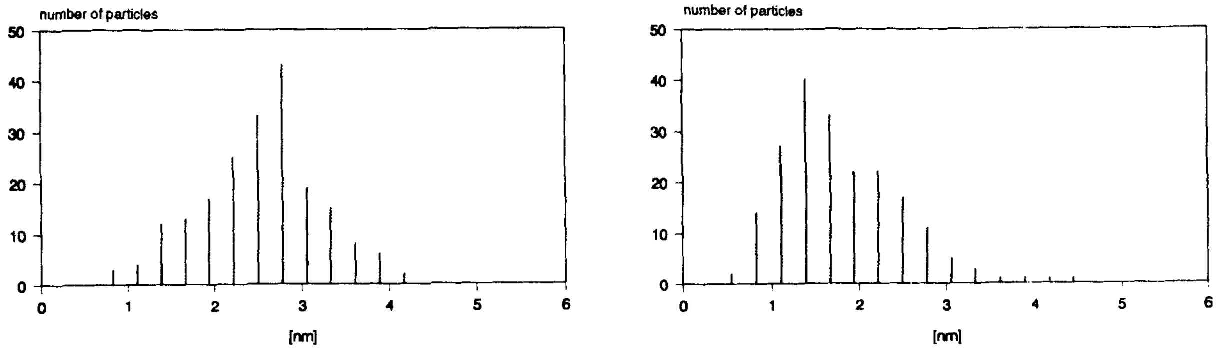
[a] For a typical procedure see the Experimental section.

to of NR_4^+-stabilized Pd(0) colloids are summarized in Table 3.

NR_4^+-stabilized palladium colloids as precursors for hydrogenation catalysts

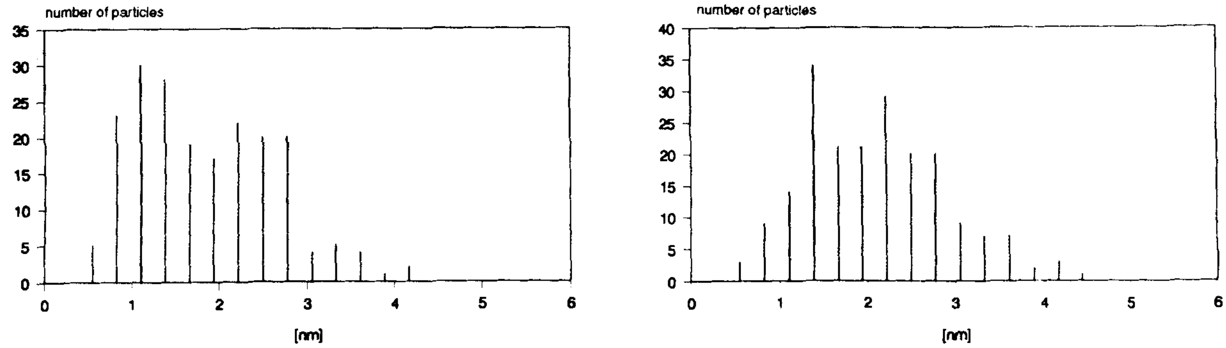
The activity, selectivity and durability of the palladium colloids as liquid-phase hydrogenation catalysts, in free or supported state (5% metal on charcoal), was evaluated by applying well-established standard tests which are routinely employed in industry for commercial catalysts.

In the homogeneous phase, the catalytic activity of different palladium colloids was measured for the hydrogenation of cyclohexene in THF; the properties of the heterogeneous Pd/C systems were tested in the hydrogenation of cinnamic acid. The experimental set-up and standard test conditions have been described elsewhere.[58,59] Based on the hydrogen consump-



a) colloid C09

b) colloid C11



c) colloid C12

d) colloid C13

Figure 8 Particle size distribution of palladium colloids prepared from $Pd(ac)_2/N(dodecyl)_4Br$ by reduction with (a) hydrogen, (b) BEt_3 or (c) HCOOH, or through (d) thermal decomposition (see Table 2).

tion in the first 5 min, the activity of the catalyst was calculated in terms (N ml g^{-1} min^{-1}).

The selectivity was derived from the product distribution based on GC analyses of a sample taken at the end of the test.

Stability was determined by the consumption of hydrogen which was supplied automatically.

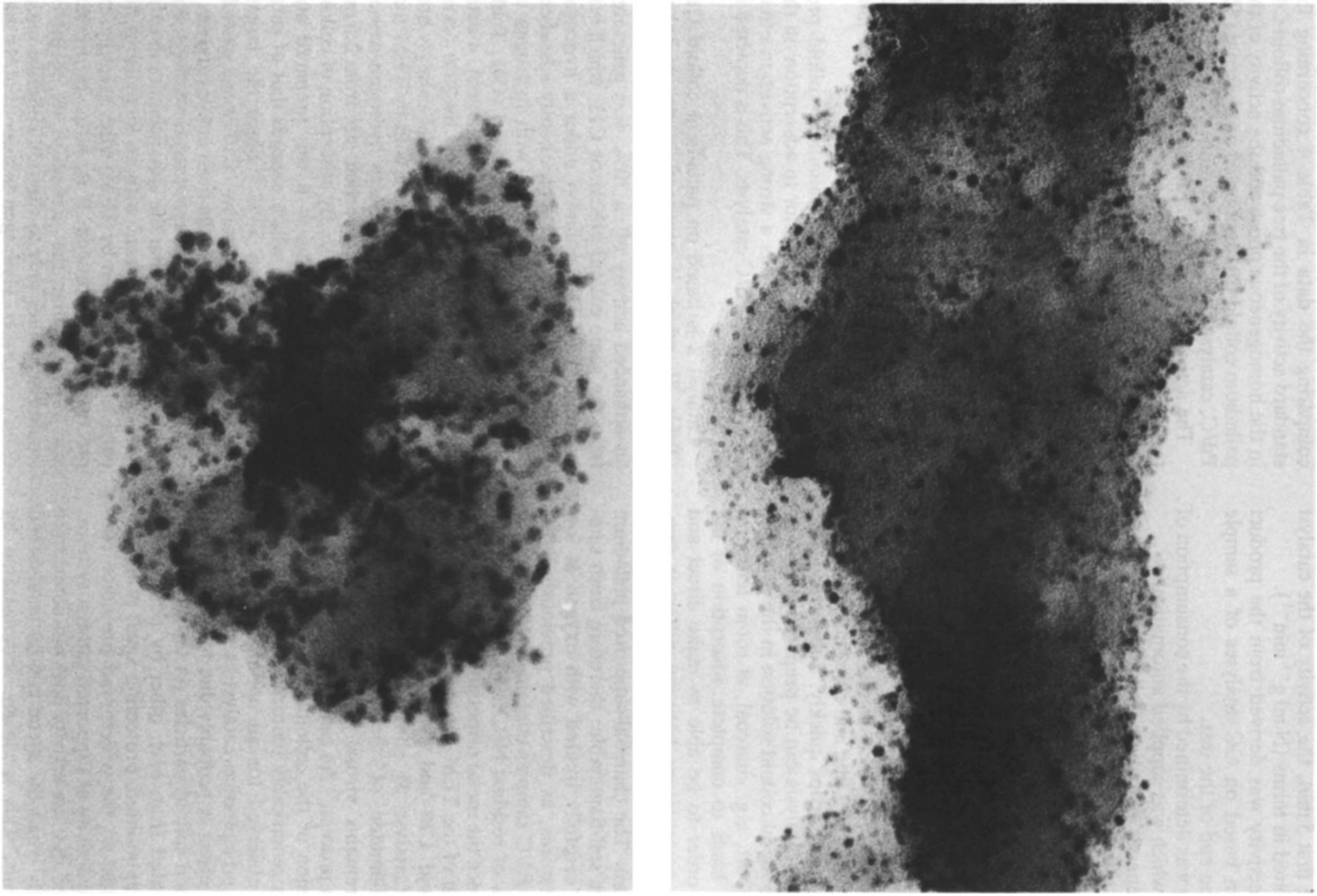
Homogeneous palladium colloids may be useful for the selective hydrogenation of unsaturated natural products such as soya-bean oil. A systematic investigation[59] has revealed that neither the preparation method (Fig. 4 or Eqn [2]) nor the particle size of the free colloid had an influence on the catalytic activity measured in the cyclohexene test. However, an anionic influence was observed; a marked decrease in activity was noted, in the order Br>Cl>ac>I. The non-supported palladium colloids agglomerate very easily in solution, which causes metal precipitation after only 6–7 min and consequently by the catalytic activity drops quickly. Supported palladium colloid catalysts can be prepared simply by stirring the metal colloid solution in the presence of the support, e.g. charcoal, at room temperature. This leads to complete adsorption of the metal. In order to be able to make direct and conclusive comparisons between different samples, we prepared each catalyst to contain 5 wt% of palladium. The charcoal-supported palladium colloids are self-flammable; therefore fresh samples were carefully treated with oxygen at low partial pressures, as described previously.[57,60,61] The dried Pd/C samples contain *ca* 10% of THF and *ca* 5% of residual NR_4X, which may positively influence the metal dispersion (see below). A comparison of the TEM images of the free palladium colloid **C10** and 5% **C10** supported on charcoal (catalyst **3**) showed that the mean particle diameter of the colloidal precursor (4.0 nm) remains virtually the same after the adsorption process.[69] As can be seen in Fig. 9(a), the dispersion of the colloidal palladium on the charcoal is remarkably uniform and comparable with that observed for an optimized industrial palladium precipitation catalyst as shown in Fig. 9(b). This effect is probably due to the fact that the adsorbed colloid particles on the surface are well separated from each other by the residual tetra-alkylammonium protecting agent present.

In contrast to the widespread prejudice concerning the activity of supported catalyst systems, it was found that the activity does not deteriorate dramatically when the metal colloid is adsorbed to a support. This is clearly demonstrated by comparing the data in Table 4 concerning the standard activity of the free palladium colloid **C01** in the homogeneous phase and the activity of the palladium colloid **C01** supported on charcoal (5% Pd/C, catalyst **1**) in THF solution.

The activities quoted in Table 5 (cinnamic acid test) of the supported Pd/C catalysts prepared on the basis of the colloids **C01**, **C12**, **C11**, **C13** (Table 3) are comparable with those of industrial catalysts. The Pd/C catalysts prepared from the colloids **C09** and **C10** (Table 3), however, show substantially higher activities in the standard test. The standard activity of the Pd/C catalyst based on the colloid **C10** (Table 3) surpasses, by a factor of 2.3, the activity of the industrial Pd/C catalyst manufactured by conventional methods. Comparative experiments have further shown that purification of the raw palladium colloids from excess NR_4X has no influence on the final catalytic activity.

After-treatment of the palladium colloid precursors with hydrogen prior to adsorption on the support, however, has a strong activation effect on the resulting Pd/C catalysts. This is depicted in Fig. 10.

Catalyst **2** is based on palladium colloid **C13** (Table 3), which is prepared in the complete absence of hydrogen; and catalyst **4**, which shows an enhanced activity of *ca* 30%, was generated from the same colloid precursor **C13**, which was maintained in THF solution under a hydrogen atmosphere for 16 h and subsequently adsorbed. Similarly, the after-treatment with hydrogen of the colloidal precursor for catalyst **1** (**C01**, Table 3) yields, after adsorption onto charcoal, a catalyst showing an activity enhanced by 20% (catalyst **5**). In the case of the colloidal catalyst precursor **C01** (Table 3), it was found by TEM that the subsequent treatment with hydrogen caused an increase of the mean particle size from 2.5 nm in **C01** to 3.2 nm in **C02**. By adsorption of colloid **C02** on charcoal, catalyst **6** was prepared and exhibited an activity which exceeds that of catalyst **1** by more than 30%.[70] Since the largest colloidal palladium precursor, **C10** (mean particle diameter 4.0 nm), gives the most active catalyst, **3** (see Tables 2, 3, 5 and Experimental section), it is plausible to assume that the enhancement in catalyst activity is correlated with an increase in the particle size (as seen by TEM) after treating the precursor with hydrogen. It is, however, necessary to stress that the activation by hydrogen treatment applies only to the free colloidal palladium precursors. Hydrogen treatment of the pal-



(a) (b)

Figure 9 TEM image of (a) palladium colloidal catalyst **1** (see Table 2) and (b) an industrial catalyst.

Table 4 Comparison of the catalytic activity of free and supported palladium colloid catalysts (5% Pd/C)[a]

Catalyst	Preparation method for the colloid	Support	Solvent	Substrate	Activity ($Nm\,g^{-1}\,min^{-1}$)
$PdCl_2/N(octyl)_4BEt_3H$(**1**)	Experimental (**C01**)	—	THF	Cinnamic acid[b]	329
$PdCl_2/N(octyl)_4BEt_3H$(**1**)	Experimental (**C01**)	Charcoal	THF	Cinnamic acid	207

[a] Based on the weight of palladium used. [b] For the test procedure see Ref. 59, pp. 162, 173.

ladium colloids already supported on charcoal leads to a sharp decrease in catalytic activity.

Earlier we reported a strong activation effect involving the doping heterogeneous Rh/C hydrogenation catalysts with low-valent titanium.[57, 60, 61] We observe here, too, that pretreatment of the charcoal support with small amounts of zero-valent titanium, in the form of either bis(η^6-toluene) titanium or $[Ti \times 0.5\,THF]_x$,[59, 71] also considerably enhances the activity of colloidal Pd/C catalysts.

As can be seen from Fig. 11, pretreatment of the charcoal surface with 0.2% low-valent titanium from different sources results in a strong activation of the Pd/C catalysts. Catalyst **9**, however, is obviously poisoned by iodide. In order to check whether the so-called 'strong metal–support interactions' between the low-valent titanium species and palladium particles, or simply the creation of acid centers on the surface, causes the activation of the catalyst, the charcoal was, in a counter-experiment, pretreated with aqueous $HCl/TiCl_3$. Since pretreatment with acid resulted in a maximum of activation (catalyst **10**), the observed doping effects with titanium are probably also affected by acid microcenters generated on the surface.

Selectivity control is an important goal in catalysis research. Conventional palladium catalysts have been modified for the selective hydrogenation of dienes and alkynes.[72–76] We have compared the selectivity of optimized industrial Pd/C catalysts with our palladium colloid/charcoal systems in the partial hydrogenation of 1,5-cyclooctadiene (1,5-COD) giving cyclooctene. As shown in Scheme 1, the diene is hydrogenated stepwise at the palladium catalysts, giving cyclooctane via a cyclo-octene intermediate. Furthermore, in the presence of hydrogen, isomerization of the initial 1,5-diene takes place,[77–79] which is important because the rate of hydrogenation for different dienes, according to Refs 72 and 73, increases in the order: 1,5-COD < 1,4-COD < 1,3-COD. Because the hydrogenation rate of the dienes is considerably higher than that of the monoene (see the Experimental section), a quick hydrogen uptake is observed initially in the selectivity test and later a sharp decrease in uptake is noted, an indication that most of the cyclooctadiene has been converted. The palladium colloid/charcoal catalyst **3** (based on the precursor **C10**; Table 3) shows a cyclo-octene selectivity of 94.5%. For comparison, using industrial Pd/C catalysts, e.g. Degussa E10 R/D or Degussa E101 B/W, the cyclo-octene selectivity was found to be 95.6% and 95.9%, respectively. So the selectivity of the palladium colloid-based catalysts is obviously quite comparable with the optimized industrial systems. However, the palladium colloid catalyst **3**, for example, was proved to be 2.3 times more active in the 1,5-COD hydrogenation than the industrial standard catalysts.

Table 5 Catalytic activity of supported colloidal palladium (5% Pd/C) in the cinnamic acid test[a]

Catalyst	Colloid precursor	Activity $N\,ml\,g^{-1}\,min^{-1}$
Pd on C (industrial)[b]	—	356
$PdCl_2/N(octyl)_4BEt_3H$ on C (**1**)	Experimental (**C01**)	406
$Pd(ac)_2/N(dodecyl)_4Br/H_2$ on C	Experimental (**C09**)	586
$N(octyl)_4PdCl_2Br_2/H_2$ on C (**3**)	Experimental (**C10**)	826
$Pd(ac)_2/N(dodecyl)_4Br/BEt_3$ on C	Experimental (**C11**)	389
$Pd(ac)_2N(dodecyl)_4Br/HCOOH$ on C	Experimental (**C12**)	401
$Pd(ac)_2/N(dodecyl)_4Br$/125 °C on C (**2**)	Experimental (**C13**)	310

[a] See Ref. 59, p. 173. [b] Precipitation of Pd on C.

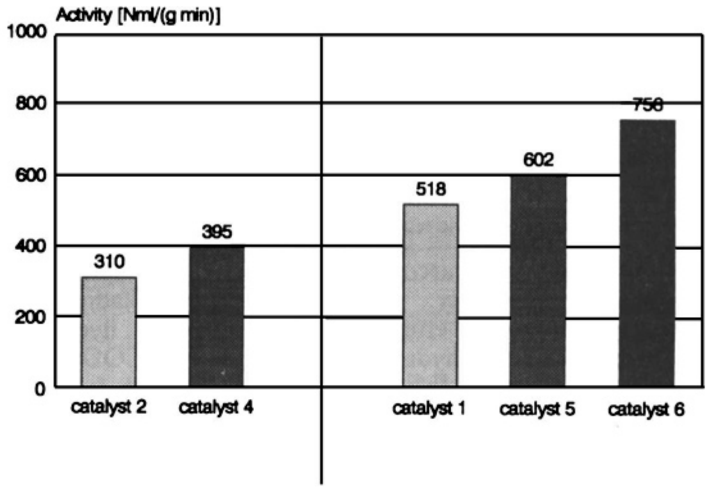


Figure 10 Effect of treatment of the palladium colloid precursors with hydrogen prior to adsorption on charcoal (for catalyst preparation, see the Experimental Section).

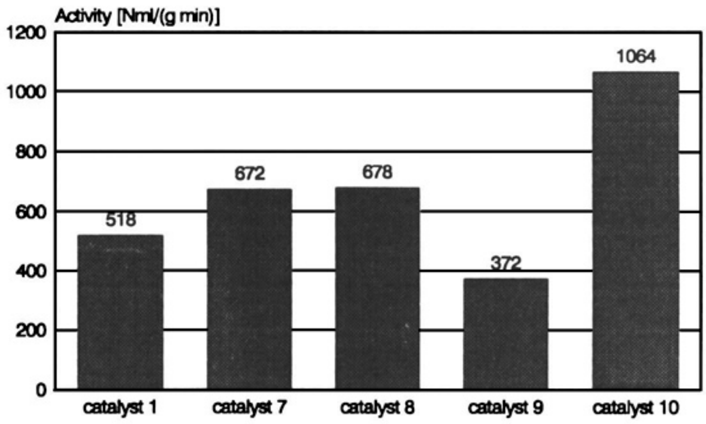
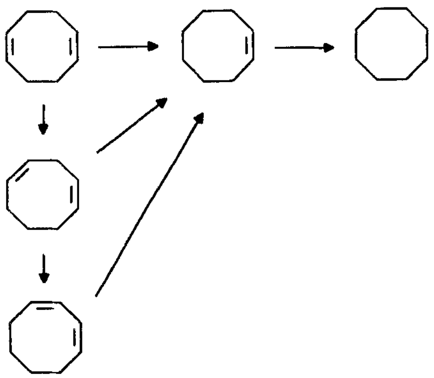


Figure 11 Activation of Pd/C catalyst based on colloid **C01** by pretreatment of the charcoal support with low-valent titanium from different sources (0.2% Ti). Dopants: **1**, no dopant; **7**, Ti × 0.5 THF; **8**, Ti(toluene)$_2$; **9**, TiI$_4$/N(octyl)4BEt$_3$H; **10**, TiCl$_3$/HCl/H$_2$O.



Scheme 1 Hydrogenation of 1,5-cyclo-octadiene.

The long-time stability of industrial and colloidal Pd/C catalysts over an extended period of time was compared by measuring the total turnover number of the systems in the hydrogenation of cyclo-octene in ethanol at 40 °C (see the Experimental section). This was exemplified with an industrial Pd/C standard catalyst (Degussa E10 R/D), the palladium colloid/charcoal catalysts **1** (based on **C01**; Table 3), **3** (based on **C10**; Table 3), **8** [based on **C01**, surface Ti(0)-doped], **11** (based on **C01**, surface HCl-pretreated). The results are summarized in Fig. 12, inspection of which shows that the various methods of pretreating the surface with titanium (catalyst **8**) or aqueous hydrochloric acid (catalyst **11**) are disadvantageous for the long-time stability of the resulting Pd/C catalysts. The optimum extended time stability was found for the supported palladium colloid catalyst **3**, which is based on the precursor **C10** (Table 3), having a mean particle diameter of 4 nm. The palladium colloid catalyst **3** still shows a residual activity of 30 N ml H_2 g^{-1} min^{-1} after 96×10^3 catalytic turnovers. The total conversion of substrate using catalyst **3** is seven times higher than in the case of catalyst **1** and surpasses, by a factor of 3.3, the less active industrial standard catalyst, which expires after 38×10^3 catalytic cycles. This combination of a maximum catalyst activity with a long catalyst lifespan disproves the general prejudice that highly active catalysts based on supported nanometal particles cannot be applied in practice because of their inherent instability.

The observed deactivation of the catalysts is certainly due to a number of causes, such as poisoning by impurities present in the substrates, migration and agglomeration of the active particles on the surface, and so on. The limited mechanical stability of the support clearly plays an important role for the long-term behavior of the catalyst: REM pictures of exhausted catalyst samples show that many charcoal pieces have been fragmented in the course of the test reaction because of the mechanical stress caused by the stirrer over an extended period of time. Examination of the TEM of an expired catalyst (Fig. 13) has further revealed that, during the reaction, numerous palladium particles were desorbed from the charcoal surface; large metal agglomerations were seen without any contact with the support.

The adhesion of the Pd colloids adsorbed onto the charcoal surface is markedly improved by maintaining the freshly prepared Pd/C catalysts under a hydrogen atmosphere.

CONCLUSIONS

The preparation methods presented here establish a straightforward route to NR_4^+-stabilized palladium colloids, which can be isolated completely redispersed, and are easy to handle in unusually high concentrations. Depending on the synthesis conditions, the mean particle diameter varies in the range of 1.8–4.0 nm. This provides a practical source for catalysts, active both in the homogeneous and heterogeneous phase. The palladium colloids may be deposited on supports with an unusual high degree of dispersion and with complete conservation of the particle size. The whole scope of possible catalytic applications has not yet been elucidated. Comparison with commercial catalysts, using industrially standard quality tests in liquid-phase hydrogenation, has shown that the new heterogeneous palladium colloid/charcoal systems offer superior properties with respect to activity and durability, and can compete well with the selectivity of optimized conventional catalysts. These results lead us to the conclusion that the concept of applying well-characterized, nanometal colloids as precursors for homogeneous and heterogeneous catalysts opens promising perspectives for rational catalyst design.

Acknowledgements The authors gratefully acknowledge the valuable support of the following scientists, companies and institutions: Dr B. Tesche, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany, for numerous

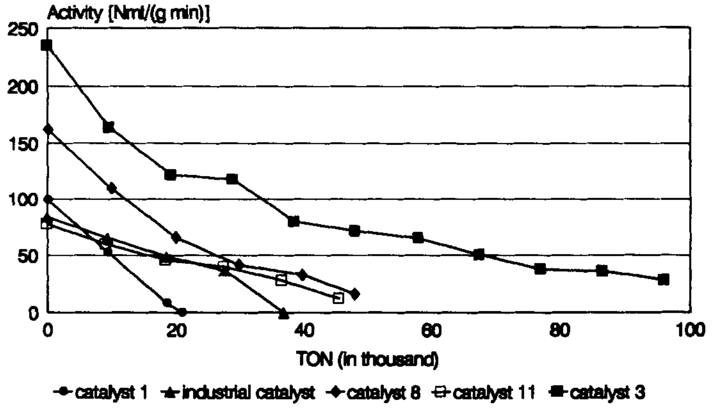


Figure 12 Stability of Pd/C catalyst in the hydrogenation of cyclo-octene.

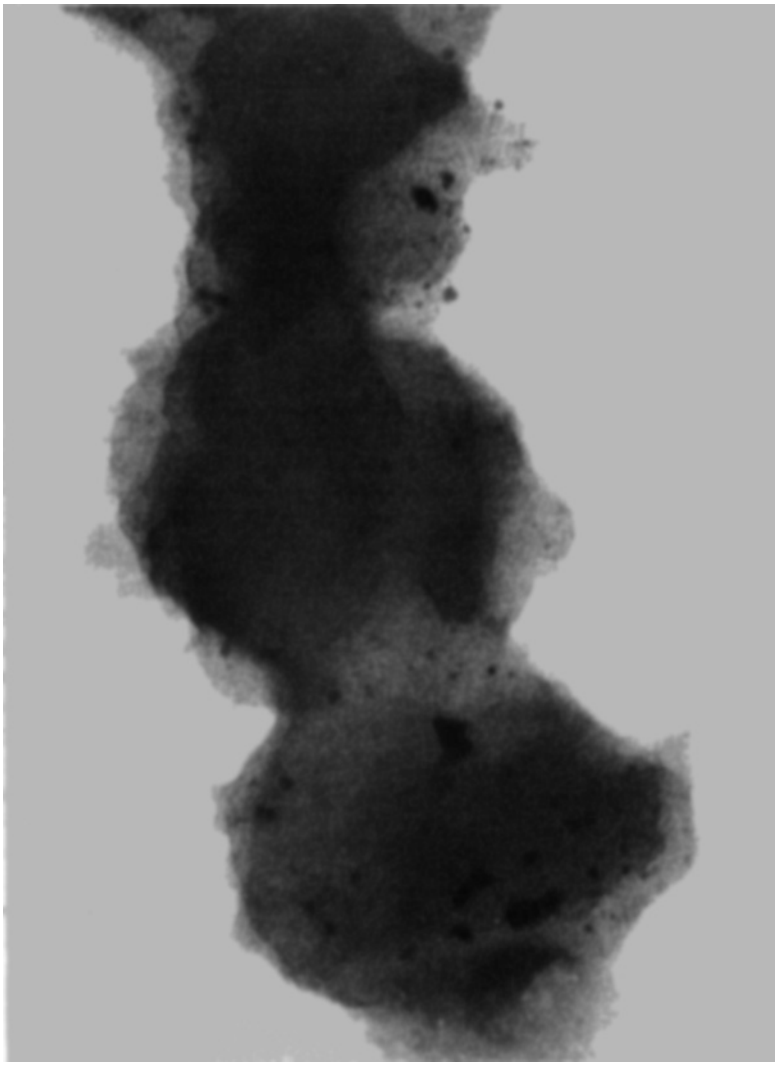


Figure 13 TEM image of the surface of an exhausted Pd colloid/charcoal hydrogenation catalyst (magnification: 360.000:1).

TEM images including Figs 9 and 13, taken with a Siemens Elmiskop 102 and DEEKO 100 at 100 kV, and many helpful discussions; Mr T. Kamino, Hitachi Instruments Engineering Co. Ltd, 882 Ichige, Katsuta-shi, Japan, for HRTEM images performed with a Hitachi HF 2000 at 200 kV including EDX point analyses; Professor Dr R. Courths and Dipl.-Phys. B. Heise, Universität-Gesamthochschule Duisburg, Germany, for XPS spectra obtained using an ESCALAB Mark II. Further, we are indepted to Professor P. Kleinschmit and Drs P. Panster and A. Freund, Degussa AG, ZN Wolfgang, Hanau, Germany, for a gift of commercial noble-metal catalysts and the test procedures for palladium/charcoal catalysts. The support of this work by Fonds der Chemischen Industrie, Frankfurt, Germany, is also gratefully acknowledged. The English manuscript was revised by Dr Lorraine Aleandri, MPI für Kohlenforschung, Mülheim, to whom the authors wish to express their sincere thanks.

REFERENCES

1. A. Behr, in *Ullman's Encyclopedia of Industrial Chemistry*, 5th ed., Vol. A18, pp. 215–246. VCH, Weinheim (1991).
2. G. W. Parshall, *Organometallics* **6**, 687 (1987).
3. J. S. Bradley, *Adv. Organomet. Chem.* **22**, 1 (1983).
4. J. S. Bradley, E. Hill, M. E. Leonowicz and H. J. Witzke, *J. Mol. Catal.* **41**, 59 (1987).
5. P. Braunstein, *Nouv. J. Chim.* **10**(7), 365 (1986).
6. H. H. Lamb, B. C. Gates and H. Knözinger, *Angew. Chem.* **100**, 1162 (1988).
7. B. C. Gates, *Catalytic Chemistry*, John Wiley, New York (1993).
8. K. Esumi, M. Shiratori, H. Ishizuka, T. Tano, K. Torigoe and K. Meguro, *Langmuir* **7**, 457 (1991).

9. K. Meguro, M. Torizuka and K. Esumi, *Bull. Chem. Soc. Jpn.* **61**, 341 (1988).
10. D. G. Duff, P. P. Edwards, J. Evans, J. T. Gauntlett, D. A. Jefferson, *Angew. Chem.* **101**, 610 (1989).
11. J. Evans, *NATO ASI Ser., Ser. C (Surf. Organomet. Chem., Mol. Approaches Surf. Catal.)* **231**, 47 (1988).
12. J. Evans, B. Hayden, F. Mosselmans and A. Murray, *J. Am. Chem. Soc.* **114**, 6912 (1992).
13. J. Evans, B. Hayden, F. Mosselmans and A. Murray, *Surf. Sci.* **279** (1–2), 159 (1992).
14. B. T. Heaton, *Pure Appl. Chem.* **60**(12), 1757 (1988).
15. R. W. Devenish, P. J. Goodhew, B. T. Heaton, C. Jacobs and S. Mulley, *Sci. Prog.* (*Oxford*) **74** (296, Pt 4), 513 (1990).
16. D. Brown, B. T. Heaton and J. A. Iggo, *Catal. Met. Complexes* **12**, 329 (1991).
17. R. W. Devenish, S. Mulley, B. T. Heaton and G. Longoni, *J. Mater. Res.* **7**(10), 2810 (1992).
18. K. J. Klabunde, Y.-X. Li and B.-J. Tan, *Chem. Mater.* **3**, 30 (1991).
19. K. J. Klabunde, *Science* **224**, 1329 (1984).
20. K. J. Klabunde and Y. Imizu, *J. Am. Chem. Soc.* **106**, 2721 (1984).
21. K. J. Klabunde and Y. Tanaka, *J. Mol. Catal.* **21**, 57 (1983).
22. K. Matosuo and K. J. Klabunde, *J. Org. Chem.* **47**, 843 (1982).
23. K. J. Klabunde, S. C. Davis, H. Hattori and Y. Tanaka, *J. Catal.* **54**, 254 (1978).
24. K. J. Klabunde, H. F. Efner, T. O. Murdock and R. Ropple, *J. Am. Chem. Soc.* **98**, 1021 (1976).
25. H. Knözinger, in *Cluster Models for Surface and Bulk Phenomena*, edited by G. Paccioni, P. S. Bagus and F. Parmigiami (Ed.) Plenum, New York (1992).
26. L. N. Lewis, *Chem. Rev.* **93**, 2693 (1993).
27. T. A. Stromnova, I. N. Busygina, M. N. Vargaftik and I. I. Moiseev, *Metalloorg. Khim.* **3**, 803 (1990).
28. I. I. Moiseev, *Pure Appl. Chem.* **61**, 1755 (1989).
29. I. I. Moiseev, *Mekhanizm Kataliza*, Chapter 1, p. 72. Novosibirsk (1984); *Ref. Zh. Khim.* Abstr. No. 4B4259 (1985).
30. I. I. Moissev, *Itogi Nauki Tekh. VINITI. Kinet. Kataliz* **13**, 21 (1984); *Ref. Zh. Khim.* Abstr. No. 16B4121 (1984).
31. A. S. Berenblyum, A. G. Knizhnik, S. L. Mund and I. I. Moiseev, *J. Organomet. Chem.* **234**, 219 (1982).
32. M. N. Vargaftik, V. P. Zagorodnikiv, I. P. Stolyarov, I. I. Moiseev, V. A. Likholobov, D. I. Kochnbey, A. L. Churilin, V. I. Zaikovsky, K. I. Zamaraev and G. I. Timofeeva, *J. Chem. Soc., Chem. Commun.* 937 (1985).
33. I. I. Moiseev, T. A. Stromnova and M. N. Vargaftik, *J. Mol. Catal.* **86**, 71 (1994).
34. G. Schmid, *Endeavour* **14**, 172 (1990).
35. G. Schmid, *Aspects Homogen. Catal.* **7**, 1 (1990).
36. G. Schmid, H. H. A. Smit, M. P. J. Staveren and R. C. Thiel, *New J. Chem.* **14**, 559 (1990).
37. G. Schmid, N. Klein, B. Morun, A. Lehnert and J. O. Malm, *Pure Appl. Chem.* **62**, 1175 (1990).
38. L. J. De Jongh, J. A. O. De Aguiar, H. B. Brom, G. Longoni, J. M. Van Ruitenbeek, G. Schmid, H. H. A. Smit, M. P. J. Van Staveren and R. C. Thiel, *Z. Phys. D: At., Mol. Clusters* **12**, 445 (1989).
39. G. Schmid, *Polyhedron* **7**, 2321 (1988).
40. L. J. De Jongh, H. B. Brom, G. Longoni, P. R. Nugteren, B. J. Pronk, G. Schmid, H. H. A. Smit, M. P. J. Van Staveren and R. C. Thiel, *NATO ASI Ser., Ser. B* (*Phys. Chem. Small Clusters*) **158**, 807 (1987).
41. G. Schmid, *Chem. Unserer Zeit* **22**, 85 (1988).
42. G. Schmid, *Kem Kozl.* **63**, 199 (1985).
43. G. Schmid, *Nachr. Chem., Tech. Lab.* **35**, 249, 252 (1987).
44. G. Schmid, *Angew. Chem.* **90**, 417 (1978).
45. G. Schmid (ed.) *Clusters and Colloids*. VCH, Weinheim (1994).
46. H. Hirai and N. Toshima, *Shokubai* (*Catalyst*) **22**(3), 190 (1980).
47. H. Hirai, H. Chawanya and N. Toshima, *Makromol. Chem., Rapid Commun.* **2**, 99 (1981).
48. H. Hirai, S. Komatsuzaki and N. Toshima, *Bull. Chem. Soc. Jpn.* **57**(2), 488 (1984).
49. H. Hirai, H. Chawanya and N. Toshima, *Nippon Kagaku Kaishi* **6**, 1027 (1984).
50. H. Hirai, H. Chawanya, and N. Toshima, *Bull. Chem. Soc. Jpn.* **58**(2), 682 (1985).
51. H. Hirai, H. Chawanya and N. Toshima, *Reactive Polym.* **3**(3), 127 (1985).
52. H. Hirai, S. Komatsuzaki and N. Toshima, *J. Macromol. Sci., Chem.* **A23**(8), 933 (1986).
53. N. Toshima and T. Takahashi, *Bull. Chem. Soc. Jpn.* **65**(4), 400 (1992).
54. N. Toshima, T. Teranishi and Y. Saito, *Makromol. Chem., Macromol. Symp.* **59**, 327 (1992).
55. H.-F. Liu and N. Toshima, *J. Chem. Soc., Chem. Commun.* **16**, 1095 (1992).
56. H. Bönnemann, W. Brijoux, R. Brinkmann, E. Dinjus, T. Joußen and B. Korall, *Angew. Chem.* **103**, 1344 (1991); *Angew. Chem., Int. Ed. Engl.* **30**, 1312 (1991).
57. H. Bönnemann, W. Brijoux, R. Brinkmann, E. Dinjus, R. Fretzen, T. Joußen and B. Korall, *J. Mol. Catal.* **74**, 323 (1992).
58. H. Bönnemann, R. Brinkmann, R. Köppler, P. Neiteler and J. Richter, *J. Adv. Mater.* **4**(12), 804 (1992).
59. H. Bönnemann, W. Brijoux, R. Brinkmann, R. Fretzen, T. Joussen, R. Köppler, B. Korall, P. Neiteler and J. Richter, *J. Mol. Cat.* **86**, 129 (1994).
60. H. Bönnemann, B. Korall, W. Brijoux, R. Brinkmann, E. Dinjus and E. Fretzen, German Patent DE 41 11719 to Studiengesellschaft Kohle mbH (1991).
61. H. Bönnemann, W. Brijoux, R. Brinkmann, E. Dinjus, R. Fretzen, Th. Joußen and B. Korall, *J. Mol. Catal.* **74**, 323 (1992).
62. I. I. Moiseev and M. N. Vargaftik. In *Perspectives in Catalysis*, edited by J. M. Thomas and K. I. Zamaraev, Blackwell, Oxford (1994).
63. G. Lagaby. In *Ullmanns Encyclopedia of Industrial Chemistry* 5th ed., Vol. A7, p. 341. VCH, Weinheim (1991).
64. B. V. Enüstün and J. Turkevich, *J. Am. Chem. Soc.* **85**, 3317 (1963).

65. J. Turkevich, P. C. Stevenson and J. Hillier, *Faraday Discuss. Chem. Soc.* **11**, 58 (1951).
66. K. Meguro, M. Torizuka and K. Esumi, *Bull. Chem. Soc. Jpn.* **61**, 341 (1988).
67. J. Kiwi and M. Grätzel, *J. Am. Chem. Soc.* **101**, 7214 (1979).
68. J. Wiesner, A. Wokaun and H. Hoffmann, *Progr. Coll. Polym. Sci.* **76**, 271 (1988).
69. H. Bönnemann, W. Brijoux, R. Brinkmann, R. Fretzen, T. Joussen, R. Köppler, B. Korall, P. Neiteler and J. Richter, *J. Mol. Cat.* **86**, 164 (1994).
70. J. Richter, Ph.D. Thesis, RWTH Aachen (1994).
71. H. Bönnemann and B. Korall, *Angew. Chem.* **104**, 1506 (1992); *Angew. Chem., Int. Ed. Engl.* **31**, 1490 (1992).
72. A. Sarkany, A. H. Weiss and L. Guczi, *J. Catal.* **98**, 550 (1986).
73. J. P. Boitiaux, J. Cosyns and S. Vasudevan, *Appl. Catal.* **15**, 317 (1985).
74. C. E. Gigola, H., R. Aduriz and P. Bodnariuk, *Appl. Catal.* **27**, 133 (1986).
75. D. Reinig, D. Hönicke and J. Gaube, *Chem.-Ing.-Techn.* **63**, 839 (1991).
76. C. Otto and J. Gaube, *Chem.-Ing.-Techn.* **61**, 644 (1989).
77. H. Hirai, S. Kamatsuzaki and N. Toshima, *Bull. Chem. Soc. Jpn* **57**, 488 (1984).
78. H. Hirai, H. Chawanya and N. Toshima, *Bull. Chem. Soc. Jpn.* **58**, 682 (1985).
79. H. Hirai, H. Chawanya and N. Toshima, *Makromol. Chem., Rapid Commun.* **2**, 99 (1981).