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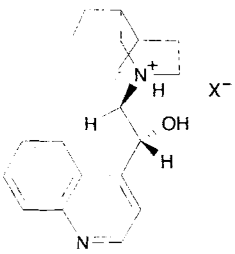
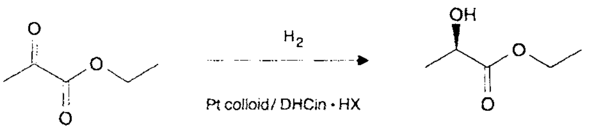
Enantioselective Hydrogenations on Platinum Colloids[**]

Helmut Bönnemann[*] and Gerhard A. Braun

Metal colloids with dimensions of a few nanometers are important for catalysis research because of their high proportion of surface atoms.[1] These colloids can either be employed as catalysts in quasi-homogeneous phases[2] or serve as precursors for heterogeneous catalysts.[3] Their stabilization in solution at concentrations necessary for catalysis is achieved by polymers,[4] ligands,[5] or surfactants.[6] In several cases it was possible to show that the stabilizer affects the catalytic selectivity.[7] Herein, we report on a chiral induction by the stabilizer in a colloid-catalyzed hydrogenation. Using as an example a platinum sol stabilized by the protonated alkaloid dihydrocinchonidine (DHCin), we examined the influence of the stabilizer on the enantioselective hydrogenation of ethylpyruvate to (*R*)-ethyllactate [Eq. (a)] in a quasi-homogeneous phase.



DHCin · HX:
X = Cl, AcO, HCO_2



(a)

The enantioselective hydrogenation of α-oxoesters on heterogeneous platinum catalysts in the presence of cinchona alkaloids was reported for the first time by Y. Orito.[8] Over the last few years, these chirally modified heterogeneous catalysts have been systematically studied with respect to catalyst preparation,[9a] catalyst structure,[9b, c, d] reaction conditions,[9e, f, g] and kinetics.[9h, i] The structure of the modifier has been varied,[10a] and the interaction between the substrate and the alkaloid has been modeled.[10b, c]

In order to synthesize colloidal platinum, an aqueous solution of a platinum salt is reduced in the presence of protonated DHCin. The normally water-insoluble alkaloid is initially transformed into the water-soluble hydroformate, and then added by syringe to an aqueous platinum tetrachloride solution. The formate reacts to yield carbon dioxide, and the resulting platinum sol (**2**) is stabilized by the hydrochloride of DHCin [Eq. (b)].

$$\mathrm{PtCl_4} + (2-n)\ \mathrm{DHCin{\cdot}HCO_2H} + n\ \mathrm{HCO_2H} \longrightarrow \underbrace{\mathrm{Pt_{colloid}}\ [\mathrm{DHCinH^+\ Cl^-}]_{2-n}}_{\mathbf{2}} + (2+n)\ \mathrm{HCl} + 2\ \mathrm{CO_2} \qquad \text{(b)}$$

$n = 0$–1.75

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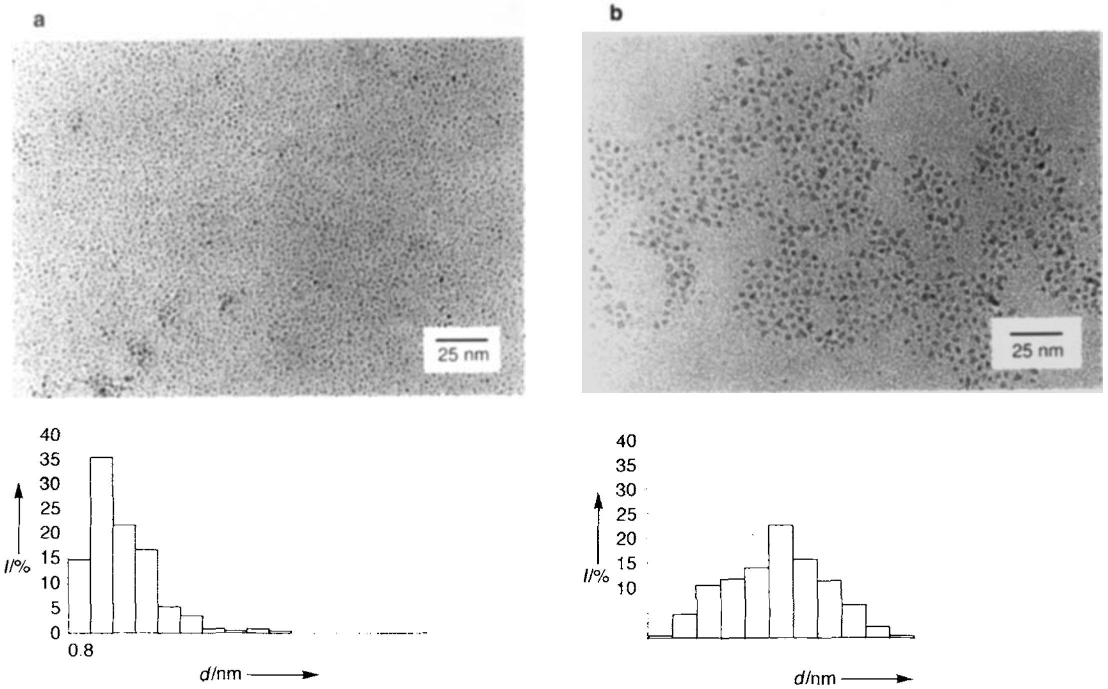

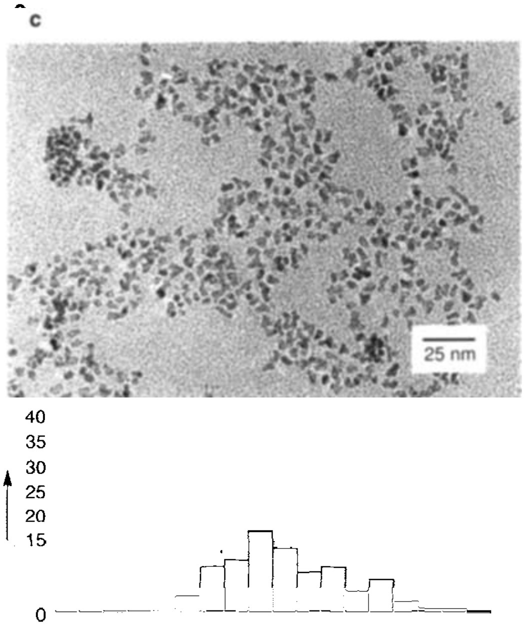

Fig. 1. Particle size distribution of DHCin-stabilized platinum colloids as a function of stabilizer concentration. Molar ratios of platinum to DHCin during the synthesis: a) 0.5, b) 1.25, c) 3.5. The distribution was determined by measuring at least 230 particles at different locations in the sample. *d* = particle diameter; *I* = relative abundance.

The colloids were examined by high-resolution electron microscopy (Fig. 1).[11] The molar ratio of platinum to dihydrocinchonidine during the synthesis determines the size of the resulting colloid; the particle size can by varied from 1.5 to 4 nm (Fig. 2).

The platinum sol (**2**) is precipitated by using sodium hydrogencarbonate, filtered off, washed, taken up in dilute acetic acid, and finally freeze-dried. The resulting black powder can be stored in the air and can be completely peptized in water or acetic acid upon the addition of methanol. The isolated platinum colloids exhibit a metal content of 40–50% by weight and are virtually free of chlorine.

The isolated platinum colloid is peptized for the hydrogenation according to Equation (a) in a 5:1 mixture of acetic acid and methanol upon addition of further DHCin. The catalysis is then performed in a quasihomogeneous phase. In general, enantiomeric excesses of about 76% were achieved.[12] Dihydrocinchonidine has a directing and a stabilizing effect: a decrease in alkaloid concentration leads to reduced activity at constant enantioselectivity (Fig. 3). This effect can be attributed to the agglomeration of the colloid in solution, which can be demonstrated by UV/Vis spectroscopic studies.[13] This agglomeration reduces only the accessible surface area, while the chiral induction at the remaining catalytically active sites is not affected. In

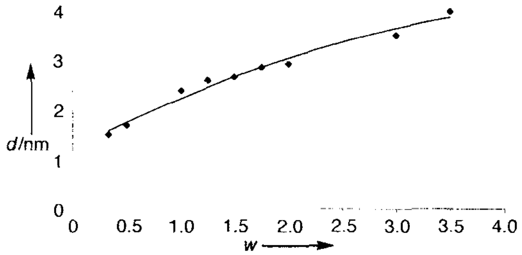

Fig. 2. Effect on particle size of the molar ratio *w* of platinum to DHCin during colloid synthesis. *d* = particle diameter.

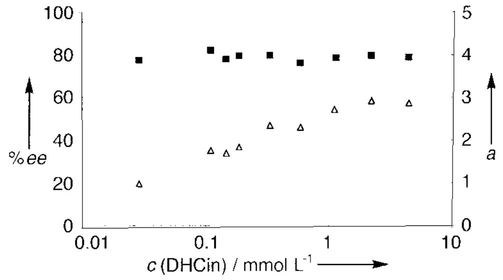

Fig. 3. Activity *a* (△) of colloidal platinum and enantiomeric excess (■) during the hydrogenation reaction (a) as a function of the concentration *c* of DHCin in the reaction medium [16].

order to avoid this agglomeration during catalysis, DHCin was added in 25 molar excess to platinum. UV/Vis spectroscopy, electron microscopy, and analytical ultracentrifuge studies before and after the reaction showed that under these conditions, no agglomeration takes place.[14] Thermostatically controlled glass reactors with flow breakers and gas addition stirrers were used for the hydrogenation. These reactors yield a very good material transport from the gas phase into the liquid. The hydrogenation was performed at 12 °C under atmospheric pressure; the course of the reaction was monitored by observing the consumption of hydrogen. Table 1 lists the colloid catalysts employed, their selectivities, as well as the turnover frequencies (TOF).

Table 1. Enantiomeric excess and TOF values for the catalytic hydrogenation according to Equation (a) on DHCin-stabilized platinum colloids of varying particle sizes.

w [a]	d_{TEM} [nm] [b]	d_s [nm] [c]	Dispersion [d]	TOF [s^{-1}]	% *ee*
0.5	1.5	2.0	0.57	1.1	76
1.25	2.6	3.0	0.38	1.1	74
3.5	3.9	4.7	0.22	0.9	78

[a] w is the molar ratio of platinum to DHCin during colloid synthesis. [b] d_{TEM} is the average particle diameter as determined by transmission electron microscopy. [c] d_s is the mean particle diameter, as averaged over the entire surface [15]. [d] The dispersion of the particles was calculated as outlined in ref. [15].

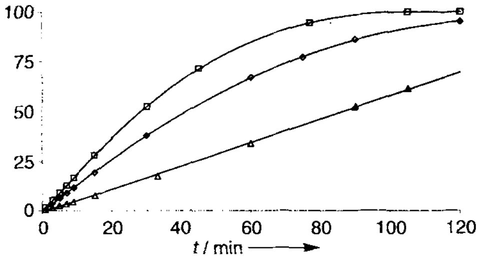

Fig. 4. Hydrogenation of ethylpyruvate on DHCin-stabilized platinum colloids of varying sizes. △: $d_{TEM} = 3.9$ nm, ◇: $d_{TEM} = 2.6$ nm, □: $d_{TEM} = 1.5$ nm [16]. The turnover [%] is plotted on the ordinate axis.

The activity of DHCin-stabilized platinum colloids decreases with increasing particle sizes (Fig. 4) as a result of decreasing dispersion. The dispersion is defined as the ratio of the number of surface atoms to the total number of atoms. It was calculated by using a surface density of platinum atoms estimated according to the method by Scholten et al.[15] and their mean diameter, as averaged over the entire surface. For the calculation of the TOF, all surface atoms were assumed to be catalytically active. The particle size had *no* effect on the TOF (Table 1) or on the enantiomeric excess (76 ± 2 % *ee*). The use of heterogeneous catalysts, on the other hand, has been reported to be associated with a distinct structure sensitivity.[9b]

DHCin-stabilized platinum colloids can be adsorbed on activated charcoal and silica. The thus obtained carrier catalysts show, for the hydrogenation according to Equation (a) at a hydrogen pressure of 100 bar in acetic acid, enantioselectivities (80 % *ee*) comparable to those reported for modified conventional heterogeneous catalysts.[9]

Experimental Procedure

Synthesis of the platinum colloid: Into a 250 mL two-neck flask, previously rinsed with aqua regia and a H_2SO_4/H_2O_2 mixture, was placed $PtCl_4$ (0.208 g, 0.6 mmol) dissolved in distilled water (160 mL). The flask was fitted with a reflux condenser and a septum, and the mixture was heated to reflux in an oil bath. During the synthesis, the bath temperature was maintained at 140 °C (± 5 °C). A solution of dihydrocinchonidine (0.355 g, 1.2 mmol) in 0.1 M aqueous formic acid (15 mL) was added rapidly by syringe. Initially, the reaction mixture became turbid and began to turn black after a few minutes. About ten minutes after the color change to black, the reaction was complete. The reaction mixture was poured into a saturated $NaHCO_3$ solution (200 mL), and the resulting precipitate was removed by a G4 fritted glass filter. The residue was washed first with a half-saturated $NaHCO_3$ solution (400 mL), then with water. The black solid was taken up in 1 M acetic acid (50 mL), and subsequently freeze-dried to remove the solvent. In this way a black powder (0.216 g) was obtained, which could be completely peptized in water and acetic acid/methanol. The metal content was found to be 41 % by weight, which indicated a yield of 71 % based on platinum. The chlorine content was below 0.5 % by weight. For the preparation of colloids with different particle sizes, the amount of platinum salt used was kept constant, while the amount of dihydrocinchonidine was reduced.

Enantioselective hydrogenation of ethylpyruvate on platinum colloids: Dihydrocinchonidine (150 mg) was dissolved in a 5:1 mixture of acetic acid and methanol (70 mL). Subsequently, platinum colloid (10 mg; particle size 1.5 nm, 41 % platinum by weight) was peptized in this solution and the dispersion was treated for 90 min in an ultrasonic bath. The resulting catalyst dispersion was a clear yellow-brown liquid. This liquid was cooled to 12 °C in a closed reactor fitted with a stirrer, degassed three times, and finally saturated with hydrogen. Using a hydrogen counterflow, ethylpyruvate (5 mL, 48 mmol) was added. The reaction was initiated by turning on the stirrer at a speed of 2000 revolutions per minute and was performed at atmospheric pressure. The course of the reaction was monitored by using the hydrogen consumption as an indicator; the reaction was complete after 120 minutes. The enantiomeric excess was determined by gas chromatography (6-*tert*-butyldimethylsilyl-2,3-dimethyl-*β*-cyclodextrin/SE54 as stationary phase) to be 76 % *ee*.

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[11] The electron microscope studies were performed with a Hitachi high-resolution transmission electron microscope, type HF 2000. The TEM samples were prepared by peptizing the colloid in water, followed by a dropwise addition of the solution onto a copper sample mesh covered with carbon. The colloidal dispersion was removed after two minutes using cellulose and the sample was transferred to the microscope. We thank the electron microscopy department of the Max-Planck-Institut für Kohlenforschung for the critical discussion of these results.

[12] a) After the study reported herein was completed, we received a personal communication form H. U. Blaser (October 5, 1995) that polyvinylpyrrolidone (PVP)-stabilized platinum colloids yield 65% *ee* for reaction (a) (at a hydrogen pressure of 100 bar and with 2-propanol as solvent). b) Collier et al. report the enantioselective hydrogenation of ethylpyruvate (up to 40% *ee* at 17% turnover) on 2-butanone-stabilized platinum colloids after the addition of DHCin. The colloids were prepared by metal evaporation and are highly agglomerated: P. J. Collier, T. Goulding, J. A. Iggo, R. Whyman in *Chiral Reactions in Heterogeneous Catalysis* (Eds.: G. Jannes, V. Dubois), Plenum Press, New York, **1995**, 105.

[13] The absorption of metal sols in the UV/Vis range is determined by the shape and size of the metal particles. The agglomeration of the colloids was confirmed by UV/Vis spectroscopy. More details about the UV/Vis spectroscopy of metal sols can be found in G. D. Duff, P. P. Edwards, B. F. G. Johnson, *J. Phys. Chem.* **1995**, *99*, 15934-15944, and references therein.

[14] The TEM studies on the agglomeration of the colloids during catalysis were performed by conserving 5 mL of the reaction solution from before and after the reaction in an aqueous solution of the polymer PVP. Details regarding the conservation of metal colloids in PVP can be found in the literature cited in ref. [13].

[15] The surface density of platinum atoms in the colloid is $\rho_s = 1.25 \times 10^{19}$ atoms per m^2, assuming equal proportions of (100), (110), and (111) surfaces: J. J. F. Scholten, A. P. Pijpers, A. M. L. Hustings, *Catal. Rev. Sci. Eng.* **1985**, *27*, 151-206. The surface-averaged diameter d_s is obtained from the expression $d_s = \sum_i n_i d_i^3 (\sum_i n_i d_i^2)^{-1}$, where n_i is the number of particles having the diameter d_i. The dispersion is calculated from $D = 6fM(\rho\sigma N d)^{-1}$, where f is the percentage of the freely accessible surface of the particle, M the relative atomic mass of platinum, ρ the density of platinum, $\sigma = \rho_s^{-1}$ the mean surface area occupied by an atom, and N is Avogadro's number: J. L. Lemaitre, P. G. Menon, F. Delannay in *Characterization of Heterogeneous Catalysts* (Ed.: F. Delannay), Dekker, New York, **1984**, 299.

[16] The hydrogenation according to Equation (a) was performed in all cases using colloidal platinum metal (ca. 4 mg), AcOH/MeOH (70 mL), and ethylpyruvate (5 mL). For the calculation of the activity a, the consumption of hydrogen per minute (in mL) was compared to the mass of platinum (in mg) employed. The hydrogen consumption during the first ten minutes of the hydrogenation reaction was used as the basis for this calculation.

Corrigendum

In the communication "Discovery of Chiral Catalysts through Ligand Diversity: Ti-Catalyzed Enantioselective Addition of TMSCN to *meso* Epoxides" by M. L. Snapper, A. H. Hoveyda, et al. (*Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1668-1671) the entries in Table 1 under the column heading "Ligand" were inadvertantly cut off. Table entries 1, 3, and 5 were obtained with ligand **10**, entries 2, 4, and 6 with ligand **15**.

Furthermore, the citations in the text beyond no. 10 are incorrect. On page 1670 they should read "... as yellow crystalline solids.[11] In a manner similar to "positional scanning",[12] ..." On page 1671 the passages should be "... enantioselectivity is improved from 40 to 86% *ee*.[13]" and in the Experimental Procedure at the top of the second column "... subjected to a ninhydrin test[14] ...".

0570-0833/96/3517-1995 $ 15.00+.25/0