Ligand Stabilized Nickel Colloids

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Ligand stabilized 4 nm nickel colloids are prepared by reduction of Ni(acac)$_2$ with Et$_2$AlH in diethyl ether in the presence of PPh$_3$; they can be isolated in solid state and redispersed in any concentration in polar solvents such as pyridine, due to their ligand shell mainly consisting not of PPh$_3$ molecules but, instead, of PPh moieties which are generated from PPh$_3$ during reaction with Et$_2$AlH with formation of free benzene.

The preparation of finely dispersed metal colloids has been the subject of numerous investigations since is known that such materials exhibit fascinating chemical and physical properties by virtue of their size.[1] Solutions of nobel metal colloids can easily be obtained by reduction of metal salts with various reducing agents in the presence of stabilizers, enforcing the stability and the narrow size distribution of the particles.[2–6] Other methods such as solvated atom dispersion in frozen solvents,[7] electrolytic reductions,[8] and the decomposition of organometallic complexes[9,10] are also effective. Once formed, these solutions can be used in homogeneous catalysis or as a source of metal particles in heterogeneous catalysis. However, such colloids normally cannot be isolated in solid state due to insufficient stabilization. Coalescence and agglomeration processes are usually observed when the solvent is removed.

During the last decade we have been successful in the preparation and isolation of various ligand stabilized noble metal colloids, both mono- and bi-metallic, and of clusters.[11,12] Clusters and colloids of less noble metals are much more difficult to generate. However since metals such as Fe, Co or Ni are of special interest due to their ferromagnetism in the bulk state, the investigation of small particles of these elements is useful in the study of the evolution of ferromagnetic properties.

The generation of naked 5 nm nickel particles by the inert gas evaporation technique has been described.[13] The reduction of nickel salts by borohydrides has variously been reported giving nickel borides.[14–17] Bönnemann *et al.* have described numerous R$_4$N$^+$-stabilized metal colloids using R$_4$NBEt$_3$H which does not form metal borides.[18–20] Here we report the generation of 4 nm ligand stabilized nickel colloids.

When Ni(acac)$_2$ and PPh$_3$ are dissolved in diethyl ether in a molar ratio of 2 : 1 and are treated with a 2-fold excess of Et$_2$AlH at −40 °C, a dark red solution of an unknown precursor species is formed which gives a black precipitate on warming slowly to room temperature.[†] The powder can be kept under an atmosphere of nitrogen for several months and can be redispersed in pyridine at any concentration. Contact with air, however, leads to spontaneous oxidation with decomposition. As expected, the solution contains Et$_2$Al(acac) and, surprisingly, free benzene, identified by gas chromatography and ^{1}H NMR spectroscopy.

HRTEM investigations[‡] of the nickel colloid, deposited on a grid from a dark brown pyridine solution, indicate very narrow particle size distribution with an average diameter of 4 nm (Fig. 1). The exact size of some of these particles can be determined by the number of visible (111) layers. Most show between 19 and 21 atomic rows, corresponding to a particle size of 3.9 to 4.3 nm. A magnified image of a colloidal particle consisting of 21 (111) layers is shown as in insert to Fig. 1.

Whilst the characterization of the colloidal metal particles has been succesful, describing the protecting ligand shell is much more difficult. Analytical investigation of various colloidal samples give values of: C, 30.0; H, 2.7; P, 9.5; Ni, 56.0% corresponding to an atomic ratio of Ni : P : C of 3 : 1 : 8. A cubic close-packed nickel particle of 4 nm diameter consists of *ca.* 3500–4000 atoms, 900–1000 of which are surface atoms. A Ni : P ratio of 3 : 1 corresponds to *ca.* 1200–1300 phosphorus atoms which must be part of the ligand shell. Furthermore, the P : C atomic ratio of 1 : 8 indicates that the P atoms must predominantly be PPh moieties (P : C = 1 : 6). If 1000 PPh groups and additionally 200 of the original PPh$_3$ ligands form the protecting shell, the P : C ratio would be the observed 1 : 8 value. However, we do not have an obvious explanation for this curious combination. Space filling models clearly demonstrate that 1000 PPh groups cannot, for steric reasons, bind directly to 1000 Ni surface atoms, either as terminal or doubly or triply bridging phosphinidene ligands. ^{31}P NMR investigations of colloidal solutions in [^{2}H$_5$]pyridine showed only a weak signal for some free PPh$_3$. Preliminary susceptibility measurements for solid colloid samples indicates a magnetic contributions of *ca.* half the value compared with that of the bulk phase.[21] This paramagnetism is obviously the reason for the lack of the observation ^{31}P NMR signals of coordinated ligands.[22]

The formation of PPh fragments and benzene can easily be understood from eqns. (1) and (2).

$$2\ \mathrm{Et_2AlH} + \mathrm{Ni(acac)_2} \rightarrow 2\ \mathrm{Et_2Al(acac)} + \mathrm{Ni} + 2\mathrm{H} \quad (1)$$

$$\mathrm{PPh_3} + 2\ \mathrm{H} \rightarrow 2\ \mathrm{C_6H_6} + \mathrm{PPh} \quad (2)$$

A preliminary explanation for the existence of such a ligand sphere could be that there are remarkable ionic interactions between positively charged nickel atoms and negatively

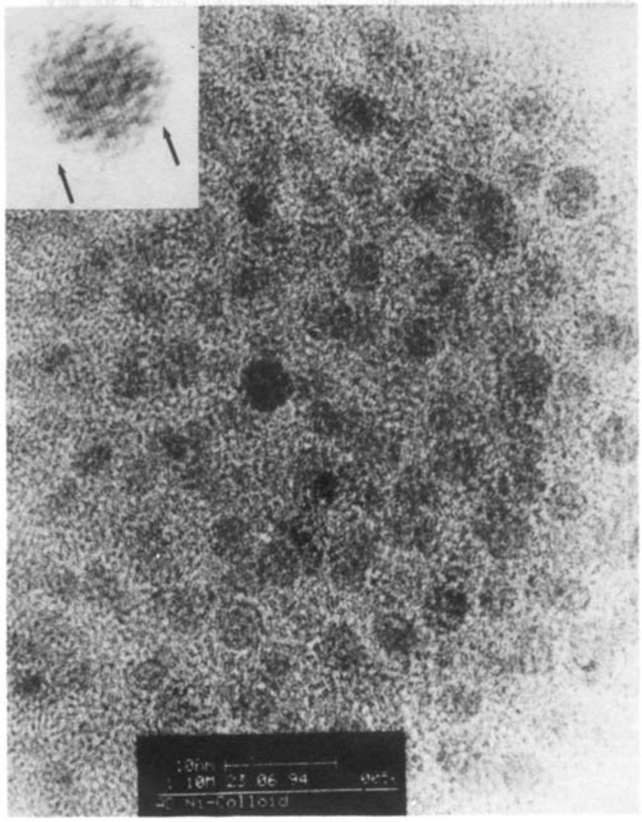

Fig. 1 HRTEM image of the nickel colloid. Some of the spherical particles show 19, 20 or 21 (111) layers, corresponding to 3.9, 4.1 or 4.3 nm diameter. Most of the particles have diameters in between this size range of 3.9–4.3 nm. The insert shows a magnified image of a single colloidal paticle consisting of 21 atomic layers.

charged PPh groups. By an ionic interaction the ligand shell can be arranged at a larger distance from the surface, enabling the addition of such a large number of PPh species. References to nickel clusters containing only PPh moieties as ligands have been found earlier, however, without any information about cluster size and structure;[21] anionic protecting spheres are quite common in colloid chemistry which allow a less ordered and less dense packed envelope around the colloid core. Solubility in only very polar solvents such as pyridine supports the supposition of ionic nickel–phosphorus interactions.

Preliminary studies of the catalytic properties of the nickel colloids show very low activities in hydrogenation reactions. For instance, the turnover frequencies for the hydrogenation of hex-2-yne to *cis*-hex-2-ene in a heterogeneous reaction is only *ca.* 2 $\text{mol}_{\text{prod}}\ \text{mol}_{\text{Ni}}^{-1}\ \text{h}^{-1}$), compared with values of some hundreds using common hydrogenation catalysts of nickel or palladium. The selectivity, however, is found to be >90%. We explain this lack of catalytic activity by the almost completely perfect protecting ligand shell covering the surface nickel atoms.

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Footnotes

† 2.0 g (7.8 mmol) of $Ni(acac)_2$ and 1.0 g (3.8 mmol) of PPh_3 were dissolved in 200 ml of absolute diethyl ether. After cooling the solution to −40 °C, 3.3 ml (31.2 mmol) of Et_2AlH was added dropwise with stirring. The solution turned dark red. After 1 h at −40 °C the homogeneous solution was slowly warmed to room temp. leading to a black precipitate which was filtered and washed several times with ether and then dried under vacuum to give 0.9 g of the colloid.

‡ The HRTEM images were recorded on a Philipps-CM 200 FEG electron microscope operating with a Supertwin lens at 300 keV.

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