

Transferring Colloidal Metal Particles from an Organic to an Aqueous Medium and *vice versa* by Ligand Coordination

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Colloidal noble metal particles dispersed in an organic medium have been transferred to an aqueous medium, and then transferred back to an organic medium by using a coordination capture technique.

In recent years much work has focused on colloidal metal particles or metal clusters, which have extremely different chemical and physical properties from those of both atomic and bulk metals.¹ Colloidal dispersions of noble metal clusters act as active and selective catalysts not only for common organic reactions² but also for visible light-induced hydrogen evolution,³ which is not successful with supported metal catalysts. Colloidal dispersions of metals have usually been prepared in an aqueous phase. Recently dispersions in organic phases have received attention in order to attain high catalytic activity.⁴ However, metal dispersions in an organic phase must be prepared in the organic solution by reduction of metal ions.

Soluble ligands are often used for the extraction of metal ions or metal complexes. Even the large gold complex cluster $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$ can be solubilized into water by ligand exchange with water-soluble ligands.⁵ There have been a few reports on the coordination of organic compounds to colloidal metals, especially noble metals. Poly(*N*-vinyl-2-pyrrolidone)-protected palladium colloids are stabilized in an aqueous medium by coordination of the polymer.⁶ Aqueous dispersions of gold colloids can be stabilized by a water-soluble phosphine ligand.⁷ Noble metal colloids can be immobilized on solid supports having sulfur or phosphine ligands.⁸ To the best of our knowledge, there has been no report on the transfer of colloidal metal particles from an aqueous phase to an organic phase or *vice versa*, although the extraction of metal ions or metal complex is well known.

Here we propose for the first time a novel method for transferring colloidal noble metal particles from an organic phase to an aqueous phase and *vice versa* by using soluble organic ligands.

Stable dispersions of palladium colloids in methyl isobutyl ketone (MIBK, 3,3-dimethylbutan-2-one) were prepared by the thermal decomposition of palladium acetate in MIBK.⁹ In order to transfer the colloidal palladium particles from the MIBK phase to an aqueous phase, the water-soluble phosphine ligand, sodium diphenylphosphinobenzenesulfonate (DPPS), was used. When 10 cm³ of 0.5 mmol dm⁻³ palladium dispersion in MIBK was treated with the same volume of 1.4

mmol dm⁻³ DPPS solution in water, the palladium colloids were not transferred from the MIBK phase to the aqueous phase, but formed flocculates in > 95% yield. In contrast, on treatment with a 93 mmol dm⁻³ DPPS solution, the palladium colloids were directly transferred to the aqueous phase (which we term direct extraction). The resulting dispersion was quite stable. The UV-VIS spectra before and after the extraction were quite similar to each other, having just end absorption without a peak, which indicates that these solutions do not contain any metal ion or complex, but only the dispersed metal colloids. The UV-VIS spectra measured before and after the transfer experiments demonstrate that the transfer rate of the colloids was >95%. Fig. 1 shows the dependence of the absorbance of the extracted palladium dispersion at 500 nm upon the concentration of DPPS in water, and clearly demonstrates that a particular concentration of DPPS is necessary for optimum extraction of the palladium colloids in the present system.

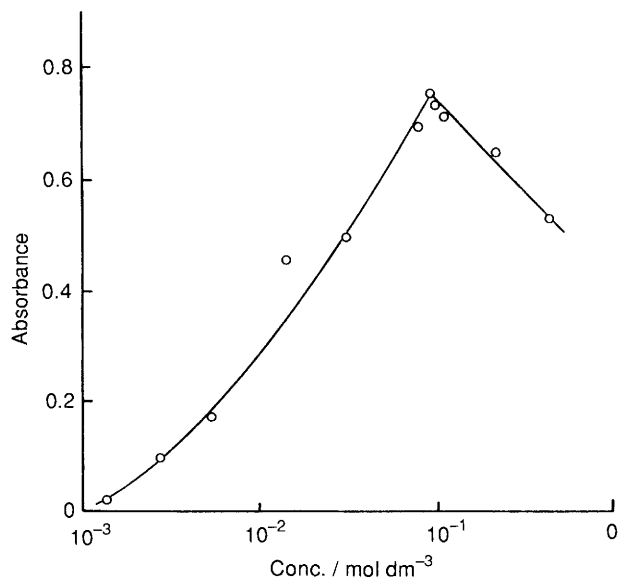


Fig. 1 Dependence of the absorbance of the extracted palladium dispersion at 500 nm upon the concentration of DPPS in water; the maximum transfer percentage is > 95%

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The flocculates of the palladium colloids produced on the interface by treatment of the MIBK dispersion with an aqueous solution of DPPS of low concentration were separated from the solution by centrifugation, and washed with acetone. The separated colloidal particles can be dispersed in pure water, resulting in the dispersion of palladium. The dispersions can be stabilized by addition of small amounts of DPPS. This procedure can form an aqueous dispersion of DPPS-protected palladium colloids as a result (which we term indirect extraction). The particles of the colloidal dispersions were studied by electron microscopy. The average diameters, with standard deviation in parentheses, of the particles before and after the extraction were 2.3(0.68) nm and 2.5(0.81) nm, respectively, which indicates that almost no change occurs after the extraction treatment.

Colloidal dispersions of platinum were easily prepared by photo-irradiation of a 1.0 mmol dm⁻³ H₂PtCl₆ solution in water-ethanol (1:1 v/v) in the presence of poly(*N*-vinyl-2-pyrrolidone) (PVP).¹⁰ Evaporating the solvent from the dispersions and then redissolving the residues in pure water gave stable aqueous dispersions of PVP-protected platinum colloids at the same concentration. The indirect method was applied to the resulting dispersions for transferring the platinum colloidal particles from the aqueous phase to an organic phase. Treatment of the 1 mmol dm⁻³ platinum aqueous dispersion with a toluene solution (15 mmol dm⁻³) of triphenylphosphine (TPP) produced flocculates of the colloids in >95% yield. The flocculates, after separation by centrifugation, were washed with a small amount of acetone and then dispersed in the same volume of butanol, resulting in a stable dispersion of the platinum colloids without any additive. The average particle size (diameter) and size distribution (standard deviation) of the resulting platinum colloids in butanol, measured by transmission electron microscopy (TEM), were 2.1 and 0.32 nm, respectively, which are nearly the same as those originally prepared by photo-irradiation (2.1 nm and 0.28 nm, respectively). This observation demonstrates again the quantitative transfer of the particles by the present procedure. Decanol, and the mixed solvents butanol-MIBK (1:9 v/v) and butanol-toluene (1:9 v/v), instead of butanol, can also be used to produce the stable dispersions.

The resulting dispersion of platinum colloids in butanol can be transferred back to the aqueous phase by treatment with the same volume of 1.4 mmol dm⁻³ DPPS solution in water in >95% yield. Again the average size (2.0 nm) and standard deviation (0.28 nm), measured by TEM, indicated no change in particle size and size distribution. Identical reversible transfer of colloidal particles between the aqueous and the organic phase was successfully carried out for rhodium, palladium and gold colloids also.

This novel method to transfer colloidal noble metal particles between an aqueous and an organic medium can be performed

using not only phosphine ligands but also sulfur-containing ligands such as sulfide and thiol. Investigations on the transfer mechanism and catalytic properties of the transferred metal colloids are now in progress.

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