

Palladium Colloids Stabilised in Polymer

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Colloids have been known about for centuries, and studied since the nineteenth century, but recent developments in technology have allowed for improved and more versatile systems. For instance, the stability of colloids is now achieved through surface functionality. The high value of the surface area to volume ratio of metal colloids makes them highly attractive for catalysis applications and the surface functionality prevents their aggregation. Surface functionality can be achieved using ligands, surfactants and polymers with specific donor atoms or chemical groupings (1). In this article the preparation of palladium (Pd) colloids stabilised with a non-ionic polymer, polyvinylpyrrolidone (PVP), see Figure 1, will be discussed (2). The Pd precursor usually forms a complex with the PVP before reduction is carried out. The colloid is then stabilised by hydrophobic interactions between hydrophobic segments of the polymer and the surface of the metal colloid, see Figure 2.

Various preparative routes may be used to synthesise Pd colloids in the PVP matrix. One of the simplest ways is by alcoholic reduction in aqueous solution in the presence of PVP and gentle heating. The use of alcohol as a reducing agent offers the advantage that the residues are simple organic compounds, unlike the residues of other reducing agents such as borane types.

Although this preparative path is simple, a

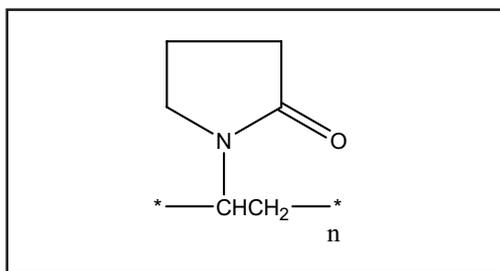


Fig. 1 Polyvinylpyrrolidone (PVP)

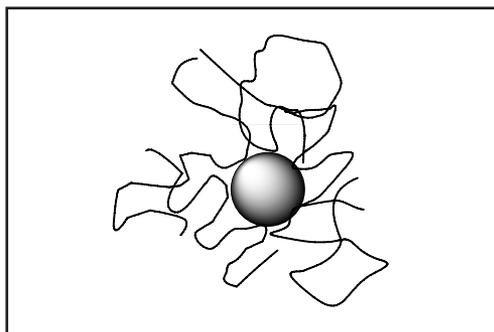


Fig. 2 A colloidal Pd particle stabilised in a polymer matrix

number of variables and parameters may influence the characteristics of the end product. These include reaction conditions (for instance, reaction temperature and time), the quantity and molecular weight of the PVP, the polymer to metals ratios, as well as the metal precursors or pH of the initial solution. These parameters will affect mainly the particle size of the Pd colloid and its distribution within the polymer, see Figure 3.

A range of Pd precursors is available and it was found that solubility of a precursor in the reaction mixture is not a prerequisite. For instance, $\text{Pd}(\text{CH}_3\text{CO}_2)_2$ showed partial solubility in a 50/50 EtOH/H₂O solution at room temperature. Upon heating, subsequent dissolution and reaction yielded colloidal Pd. Some literature preparations (2, 3) used H_2PdCl_4 as the precursor in specific concentrations, and the pH of the reaction mixture was changed by addition of NaOH (2). It was noted that the particle size distribution of the colloidal solution decreased with increasing pH. A suitable amount of base in the reducing system produced an increase in the reduction rate, thus leading to smaller particle size colloids.

The metal to PVP ratio influences the size and particle size distribution of the colloidal species. The general trend shows that a low ratio (large quantities of PVP) gives rise to a monodispersed

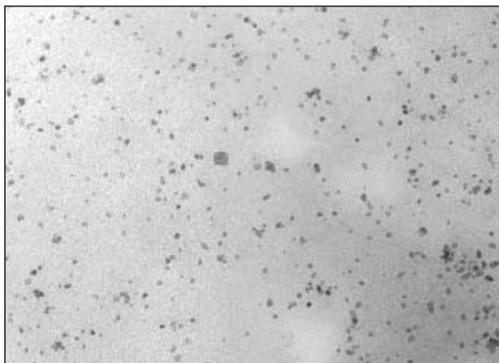


Fig. 3 A typical distribution (1–10 nm) of a Pd colloid in a polymer matrix

colloidal species while a high ratio yields a wider particle size distribution, that is, small particles are present as well as larger ones.

A wide range of short chain alcohols may be used for such experiments. As their boiling points will influence their reducing abilities it is difficult to rationalise their effects. However, for a given alcohol and concentration, an increase in temperature will induce crystal growth and result in the formation of larger particles (2, 3).

It is interesting to note that the reverse effect is observed when Ru(III) salts are reacted in polyols in the presence of PVP. This study showed that more nuclei are formed at higher temperatures and in a short period of time, and in turn the growth in size of the particles is hindered (4). The long alkyl chain of the polyol may have an important effect on the rate of the reaction as well as on the heating rate, since, in another study, the reduction of Pd in the presence of PVP with ethylene glycol showed that an increase in temperature yielded more sintered particles (3(b)). Other factors, such as the heating rate, will have a large effect on the resulting colloid; for instance, a study on a wide

range of metals, including Pd, showed that microwave heating yielded smaller sized particles compared with oil bath heating (slower heating rate) (5).

These Pd colloidal materials ought clearly to find use in catalysis. Indeed, a number of papers reporting their activities in a range of reactions have been reported (6). However, in order to optimise activity and selectivity of these colloidal material as catalysts, further work is needed to manipulate and control the size and the morphology of these colloids and understand the relationship between their characteristics and activity.

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The Most Commonly Used Platinum Group Metal Salts

The most commercially used pgm salts are generally their chlorides. Their main uses are: chloroplatinic acid – as a precursor for loading platinum onto substrates for heterogeneous catalysts; palladium chloride – for electronic plating; rhodium trichloride – for plating applications and catalyst loading; chloroiridic acid – for plating, especially for anode coatings for chlor-

alkali use; osmium tetroxide – in electron microscopy; and ruthenium trichloride – for plating, especially for anode coatings for chloralkali use.

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