

Synthesis of a Stable Platinum Organosol and its Application for Reduction of Nitrobenzene to Aniline

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The first example of the synthesis of a platinum organosol stable to air and aqueous acidic conditions is described and the exploitation of its high activity as a practical hydrogenation catalyst is illustrated in the reduction of nitrobenzene.

There has been much recent interest¹⁻⁷ in the synthesis of colloidal metal sols dispersed in organic solvents (organosols). One challenge in this area is to synthesise an organosol which is stable to air, moisture, or aqueous acidic conditions, but to the best of our knowledge examples of such stable systems are rare. Most of the metal organosols reported are stabilised by polymers (e.g. polyvinylpyrrolidone) that are destabilised on exposure to air. Stable systems have great potential as practical hydrogenation catalysts, since they would combine the high activity of the finely dispersed colloidal particles of the metal with the stability of the conventional catalysts. We now report the first example of the preparation of a platinum organosol, stable to air and aqueous acidic conditions, and its use in the reduction of nitrobenzene. The product aniline can be extracted using aqueous HCl, and the organic layer containing Pt reused.⁸

The organosol was prepared as follows: to a solution of $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ (25 mg) in water (70 ml) was added cetyl(tri-

butyl)phosphonium bromide (CTPB; 50 mg). Sodium borohydride (64 mg) in water (5 ml) was added slowly to reduce platinum to the metal oxidation state. The clear Pt sol obtained was extracted with toluene (75 ml). The aqueous layer gradually turned colourless as the metal was extracted into the organic layer. The sol was found to be stable to air and aqueous acidic conditions.

The action of the cationic surfactant CTPB seems to be unique in stabilising platinum particles. Synthesis of the sol with the surfactants cetyl(trimethyl)ammonium bromide, sodium dodecylbenzene sulphonate or the nonionic polyethylene glycol type has not been successful so far. The metal is probably more readily extracted into toluene with CTPB since this surfactant is more soluble in the organic solvent than the others tried. A combination of charge and steric factors may cause this system to be unusually stable, but the reasons for this stability need to be studied further.

Transmission electron microscopy (TEM) in combination

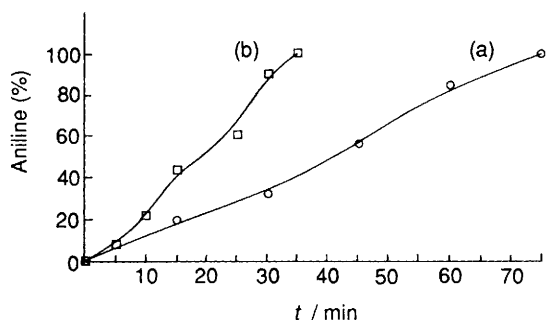


Figure 1. Reduction of nitrobenzene at 32 °C on (a) Pt/C and (b) the Pt sol: $[\text{PhNO}_2]_{\text{initial}} = 0.108 \text{ mol dm}^{-3}$ in toluene; Pt, 0.6 mol % (w.r.t. PhNO_2).

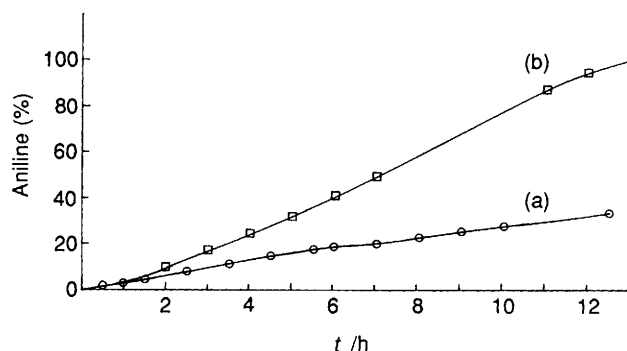


Figure 2. Reduction of nitrobenzene at 32 °C on (a) Pt/C and (b) the Pt/sol: $[\text{PhNO}_2]_{\text{initial}} = 2.7 \text{ mol dm}^{-3}$ in toluene; Pt, 0.025 mol% (w.r.t. PhNO_2).

with selected area diffraction studies were carried out using a JEOL-1200 Ex instrument (Tokyo) operating at 120 kV. The crystalline phase was identified by the Debye-Scherrer rings in the electron diffraction pattern, obtained for a sample prepared by evaporating a drop of sol on a copper grid. The particle size was in the range 25–40 Å. The calculated d spacings correspond to those for platinum metal (2.265, 1.962, 1.387 and 1.139 Å). ^{11}B NMR spectroscopy indicated the

presence of traces of boron, probably associated with platinum. The ^1H NMR spectrum of the sol showed two types of platinum hydride ($\delta -21.2$ and -43.4).

Reduction of nitrobenzene was carried out as follows: nitrobenzene (1 g) was mixed with the organosol (75 ml) and hydrogen bubbled through the mixture at 25 ml/min at room temperature (32 °C). The reaction was carried out in the presence of the aqueous layer from which the Pt had been extracted into toluene. In the absence of the aqueous layer, the metal organosol is not stable during reaction, for reasons which are not clear. Products were analysed at intervals by GC (10' OV17 column; temperature programmed from 90 to 150 °C). At the end of the reaction, the product aniline was extracted into aqueous HCl. The organosol could be reused without loss of catalytic activity.

Figure 1 compares the kinetics of reduction of nitrobenzene to aniline on the Pt organosol and 5% Pt/C (Fluka), under similar conditions. At about 20% conversion the activity of the organosol is almost 3 times that of Pt/C. Figure 2 shows how the catalysts are affected differently by poisoning due to the product aniline, in experiments using the same amount of nitrobenzene and the two types of catalyst. After 12–13 h the Pt/C catalyst gave a maximum conversion to aniline of only 33%, whereas the conversion was quantitative with the organosol, probably because the organosol metal sites are not poisoned. This leads to significant practical advantages in increasing the batch size for the organosol.

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References

- H. Hirai, M. Ohtaki, and M. Komiyama, *Chem. Lett.*, 1987, 149.
- U.S. Pat. 4,600,701, 1986, to R. O. Dejongh and C. Vandijk.
- V. M. Deshpande and C. S. Narasimhan, *J. Mol. Catal.*, 1989, **53**, L21.
- N. Yukumichi and F. Shoer, *J. Catal.*, 1981, **68**, 406.
- Y. Nakao and K. Kaeriyama, *J. Colloid Interface Sci.*, 1986, **110**, 82.
- K. Kurihara and J. H. Fendler, *J. Mol. Catal.*, 1986, **34**, 325.
- K. Meguro, M. Torizuka, and K. Esumi, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 341.
- Indian Pat. Appl. No. 1014/CAL/89.