A New Method for Immobilization of Polymer-protective Colloidal Platinum Metals *via* Co-ordination Capture with Anchored Ligands. Synthesis of the First Example of a Mercapto-containing Supported Metallic Catalyst for Hydrogenation of Alkenes with High Activity

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A poly(*N*-vinyl-2-pyrrolidone) (PVP)-protective metallic rhodium or platinum colloid interacts at room temperature with a suspension of silica gel, bearing mercapto ligands, in a 1 : 1 methanol–water system to give a well dispersed heterogeneous metallic catalyst which shows excellent activity for the hydrogenation of alkenes.

There has been much recent interest in catalysis both by metal clusters[1] and by colloidal metals.[2] These two kinds of catalyst are closely related; a finely dispersed metal colloid protected by polymers may be regarded as a macromolecular complex of metal clusters.[3] However, supported metal catalysts which allow easy separation from the reaction products as well as repeated recycling are among the most widely used catalysts both in the laboratory and in industry. In recent years intensive studies have been made using supported metal clusters as catalysts,[1,4] but reports which discuss the immobilization of polymer-protective metal colloids for heterogeneous catalysis have so far been scarce. Hirai *et al.*[5] immobilized platinum metal colloids protected by a copolymer of methyl acrylate and *N*-vinyl-2-pyrrolidone onto a polyacrylamide gel having amino groups; this was based on the reaction between amino groups in the gel and acrylate residues in the protective polymer. This method was specially designed and its application was strictly limited.

In this communication, we report a new method for immobilization of polymer-protected platinum metal colloids, *i.e.*, using the co-ordination between ultrafine metal particles and the ligands anchored on a support surface, which is expected to be of universal significance. The only prerequisite is that the co-ordination ability of the anchored ligands should be stronger than that of the protective polymers. Here we report the preparation of a colloidal metal catalyst by the capture of poly(*N*-vinyl-2-pyrrolidone) (PVP)-protective rhodium and platinum colloids (prepared similarly to the method reported by Hirai[2b]†) by mercapto groups anchored on silica (Si–SH, prepared as described in the literature).[6] The PVP-protective rhodium colloid was in a dark brown solution, narrowly dispersed, with an average diameter of 3.5 nm as determined by TEM. Si–SH gel (87 mg, S content 5.75%) was suspended in a solution of colloidal rhodium (75 ml, Rh: 0.049 mg atom). The mixture was stirred at room temperature for 2 days. Almost all the rhodium particles were immobilized onto the gel to give a dark brown supported catalyst (elemental analysis: S 4.70, N 1.65, Rh 4.79%), leaving a clear, colourless solution. No coagulation occurred during the immobilization, as verified by TEM. The supported platinum catalyst was prepared similarly from $H_2PtCl_6 \cdot 6H_2O$. If a neat silica support

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† $RhCl_3 \cdot 3H_2O$ (34.65 mg, 0.132 mmol) and PVP (8g, 71.2 mmol as monomeric residue) were dissolved in a methanol–water mixed solvent (1 : 1 by volume, 200 ml) and then refluxed for 4 h.

Table 1. Catalytic activities of immobilized colloidal rhodium and platinum catalysts for hydrogenation of alkenes.

Catalyst	Solvent	Initial rate (mol H_2/s. g atom M)[a]	
		Hex-1-ene	Cyclohexene
Si–SH–Rh	MeOH	7.9	3.7
Si–SH–Rh	$EtOH+H_2O$[c]	3.5	2.0
Si–SH–Pt	MeOH	2.1	0.18
Si–SH–Pt	$EtOH+H_2O$[c]	1.2	0.15
H–Rh[b]	$EtOH+H_2O$[c]	7.5×10^{-2}	7.2×10^{-2}
H–Pt[b]	$EtOH+H_2O$[c]	0.11	3.6×10^{-2}
Rh/C[b]	$EtOH+H_2O$[c]	3.8×10^{-2}	0.7×10^{-2}
Pt/C[b]	$EtOH+H_2O$[c]	3.2×10^{-3}	2.1×10^{-3}

[a] *Experimental conditions*: temperature 30.0 °C, total pressure 1 atm, [M] = 0.03 mM, [alkene] = 25 mM. [b] From ref. 5. [c] Component ratio: $EtOH:H_2O = 1:1$.

without mercapto ligands was used in place of the Si–SH gel, under the same conditions, no immobilization took place.

The IR spectrum of Si–SH gel showed a characteristic vibration at 2563 cm^{-1} due to the (S–H) absorption, which decreased significantly in its intensity as the supported rhodium catalyst formed. The XPS data for the PVP-protective rhodium colloid and supported colloidal rhodium were determined. The binding energy of Rh $3d_{5/2}$ in PVP–Rh and Si–SH–Rh has a value of 307.5 eV, with 3.2 eV energy width at half-maximum intensity, which indicates that the rhodium is metallic. The binding energy of S 2p in the anchored ligand Si–SH is 163.5 eV, which is comparable to that of the small molecular analogue RSH reported in literature.[7] The S 2p binding energy in Si–SH–Rh (164.1 eV) is about 0.6 eV higher than that of Si–SH or 2.8 eV higher than those of alkali mercaptides, which is expected because the electron density on sulphur is shifted to the rhodium atom for co-ordination during the immobilization. The N 1s binding energy in PVP–Rh (400.1 eV) and in Si–SH–Rh (400.0 eV) are nearly the same and about 0.6 eV higher than that in PVP (399.4 eV), which implies that a covalent bond exists between the ultrafine metallic particle and the nitrogen atom in PVP. Elemental analysis, IR, and XPS, enable the immobilization process of colloidal rhodium to be visualized as the PVP-protected rhodium particles being held separately on the silica surface by the anchored mercapto ligands.

Hydrogenation of alkenes was catalysed by the colloidal rhodium and platinum particles immobilized on silica gel having mercapto groups. The results are summarized in Table 1. For comparison, some relevant data which were obtained using Hirai's immobilized catalysts[5] are also listed. The catalysts prepared here exhibited high activities which were 10—100 times higher than the activities for Hirai's immobilized catalysts or 100—300 times higher than those of commercial Rh/C and Pt/C catalysts,[5] under the same conditions. These high catalytic activities are believed to be due to the fact that immobilization *via* co-ordination capture can create favourable conditions for easy access to the substrates, preventing the colloidal particles from aggregating and thus forming a well dispersed catalyst. The immobilized catalyst can be easily decanted from the reaction mixture, and the catalytic activity remained virtually unchanged with repeated use for the following runs. In the hydrogenation of heptene catalysed by Si–SH–Rh, for example, the catalytic activity of the fourth run was the same as that of the first run, and no metal leaching was detected.‡ The good stability of the catalyst can be rationalized since the mercapto ligands anchored on the silica surface can very strongly co-ordinate to the platinum metals.[8] Sulphur-containing compounds have been generally regarded as poisons for platinum metal catalysts; this is the first example, to the best of our knowledge, of a mercapto-containing supported metallic catalyst with high activity for hydrogenation of alkenes. Further studies are directed toward extending this procedure to other transition metals, ligands, and catalytic reactions.

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‡ The platinum content in solution was determined by AAS with a detection limit of <15 p.p.b.