In situ synthesis and the catalytic properties of platinum colloids on polystyrene microspheres with surface-grafted poly(*N*-isopropylacrylamide)‡

Chun-Wei Chen, Ming-Qing Chen, Takeshi Serizawa and Mitsuru Akashi*†

Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering, Kagoshima University, 1-21-40 Korimoto, Kagoshima 890-0065, Japan

Well dispersed platinum colloids were synthesized *in situ* on polystyrene microspheres with surface-grafted poly(*N*-isopropylacrylamide) *via* the reduction of $PtCl_6^{2-}$ by ethanol, and found to be active and stable heterogeneous catalysts for the hydrogenation of allyl alcohol in water.

There is currently much interest in the preparation of colloidal noble-metal particles with a diameter of a few nanometers or less, not only owing to their unique physical and chemical properties, but for widespread applications such as in catalysis.[1,2] The synthesis of catalytically active metal colloids by aqueous alcohol reduction of metal salts in the presence of a protective polymer was firstly reported by Hirai and coworkers.[3,4] In a proportion of cases the polymer-protected metal colloids have been immobilized on a support,[5–7] thus giving the advantages of a truly heterogeneous catalytic system. These synthesis routes are based on a two-step process involving synthesis of colloidal nanoparticles and immobilization *via* covalent interaction or ligand coordination between the protective polymers and supports. These methods obviously suffer from special design of the protective copolymer and/or complex steps for the immobilization. Here, we report an alternative approach involving the synthesis *in situ* of the platinum colloids on polystyrene microspheres with surface-grafted poly(*N*-isopropylacrylamide) (PS-PNIPAAm). The catalyst, separated from the reaction mixture by centrifugation, retains high activity on recycling in the aqueous hydrogenation of allyl alcohol.

A range of monodispersed microspheres have been prepared by emulsifier-free dispersion copolymerization of styrene with a PNIPAAm macromonomer of molecular mass 3600. The average diameter and polydispersity index of the microspheres showed here, as determined from TEM image, are 500 nm and 1.01, respectively. The PNIPAAm branches covalently attached on the surface of microspheres provide a steric stabilization for the long-term water dispersibility of microspheres. The details concerning the synthesis and characterization of such microspheres have been given elsewhere.[8] We have already reported the formation of platinum colloids with an average diameter of 20.9 Å by ethanol reduction of $PtCl_6^{2-}$ in the presence of PNIPAAm with a mean molecular mass of 4000.[9] By using the PNIPAAm branch on the surface of the microspheres as the capping polymer, we have firstly synthesized *in situ* the well dispersed platinum colloids on the surfaces of polystyrene microspheres.

The synthesis *in situ* of platinum colloids on polystyrene microspheres by alcohol reduction of $PtCl_6^{2-}$ is similar to that of PNIPAAm-protected colloidal Pt sol.[9] For example, $H_2PtCl_6\cdot 6H_2O$ (0.01 mmol Pt) and PS-PNIPAAm (45.2 mg, 0.4 mmol as PNIPAAm monomeric unit) were added in an ethanol–water mixed solvent (6/4, v/v, 38 ml), and the solution was then refluxed at 90 °C for 1.5 h. After separating the dark brown microspheres from the reaction mixture by centrifugation (7000 rpm, 10 min) and redispersing them in water, we studied the activity and stability of the Pt colloids on the microspheres for the aqueous hydrogenation of allyl alcohol.

The ESCA data for the Pt colloids on PS-PNIPAAm showed that the platinum appears to be in a zero-valent state after the recycling processes and a coordination interaction exists between the platinum colloid and the nitrogen atoms in PNIPAAm. Therefore, PNIPAAm branches of a polystyrene microsphere are adsorbed on the surface of the Pt colloids by both the hydrophobic interaction of the main chain and the coordination interaction of the amide group in the side chain. As a consequence, the strong interaction of PNIPAAm branches with Pt particles prevents or slows the migration and agglomeration of the metal particles by steric stabilization.

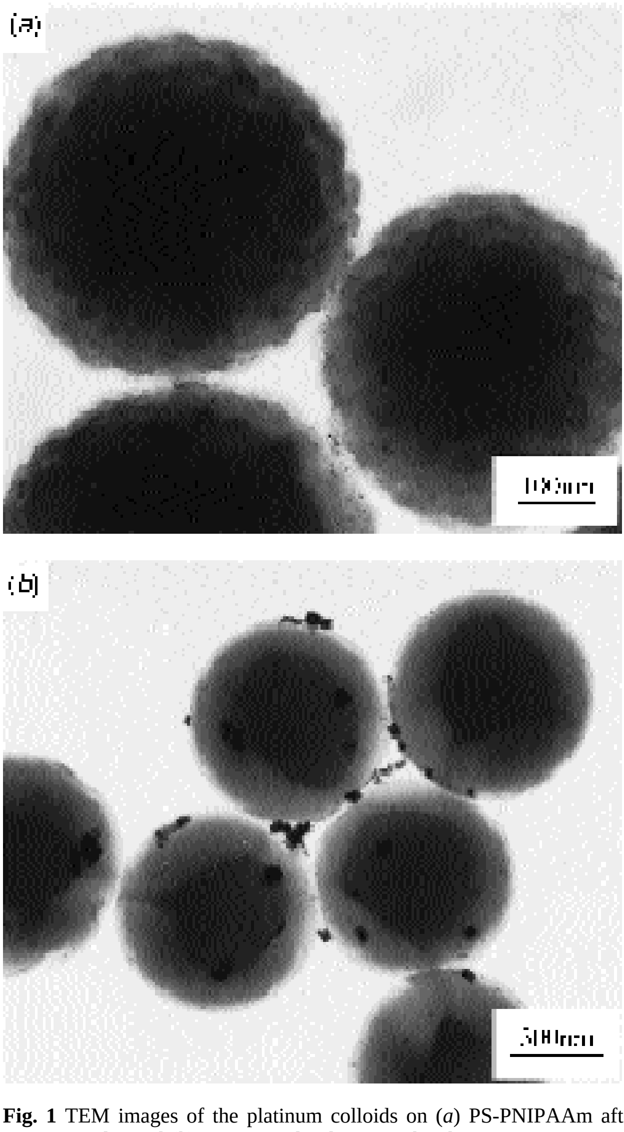

Fig. 1 TEM images of the platinum colloids on (*a*) PS-PNIPAAm after seven recycles and (*b*) commercial polystyrene beads

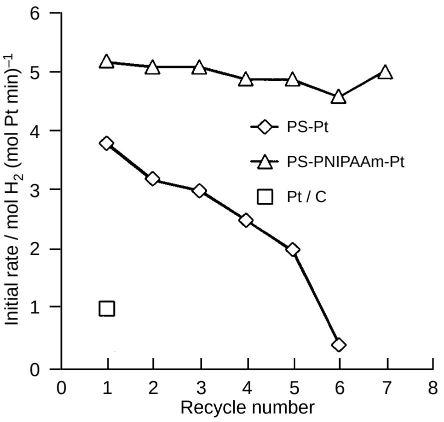

Fig. 2 Recycling of platinum colloids on PS-PNIPAAm and commercial PS beads in the hydrogenation of allyl alcohol (recovered by centrifugation). Conditions: Pt, 0.004 mmol (PS-Pt, 0.005 mmol); allyl alcohol, 2 mmol; solvent, water, 20 ml; 25 °C; H_2, 1 atm.

The PNIPAAm branches not only stabilize the platinum colloids by steric repulsion, but also immobilize them on polystyrene microspheres. TEM images of the platinum colloids on polystyrene microspheres showed that the particles have been immobilized in a well dispersed manner on the polymeric supports. The average particle size (diameter) and size distribution (standard deviation) of the fresh catalyst were 15.0 and 5.6 Å, respectively, which are smaller than those of the platinum colloids protected by free PNIPAAm (20.9 and 6.3 Å, respectively).[9] This may suggest that the migration and agglomeration of the metal colloids can be further prevented by covalently bonding the protective polymer to the surface of the polystyrene microspheres. The immobilized Pt colloids on the surfaces of the microspheres were in a very stable state and little change in the measured size distributions after seven recycling times was observed. Fig. 1(*a*) shows that the immobilized colloids are located at the surface of microspheres, and the vast majority of particles are isolated from each other after seven catalytic runs. Here, the average diameter and standard deviation of the Pt colloids are 15.2 and 5.7 Å, respectively. However, the TEM image of platinum colloids on the commercial PS beads shows that most of the Pt particles agglomerated together owing to the total lack of steric stabilization of the polymer [Fig. 1(*b*)].

The platinum colloid on the commercial PS beads or synthesized PS-PNIPAAm was employed as a heterogeneous catalyst for the hydrogenation of allyl alcohol in water. The data in Fig. 2 show the initial hydrogenation rate, with the same sample of catalyst recycled seven times. It can be seen that a PS-PNIPAAm-Pt catalyst showed higher activity than the catalysts of commercial platinum-activated carbon and Pt colloids on PS beads, and retained high activity in the hydrogenation on recycling seven times. We have previously seen the unusual temperature dependence of activity of the PNIPAAm-protected Pt sol for the same reaction.[9] The reported catalytic properties of the platinum colloids on PS-PNIPAAm in the hydrogenation are therefore most encouraging. We have evaluated thermosensitive properties of the microspheres,[8] and suggest that the activity of the catalyst must be moderated through a temperature change.

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Notes and References

† E-mail: akashi@apc.eng.kagoshima-u.ac.jp

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