The 2014 World Congress on
Advances in Civil, Environmental, and Materials Research (ACEM14)
Busan, Korea, August 24-28, 2014

Preparation of polyethyleneimine-stabilized platinum nanoparticles

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ABSTRACT

Platinum nanoparticles stabilized by linear polyethyleneimine were prepared by the liquid-phase reduction of chloroplatinic(IV) acid with sodium borohydride. The averaged radii of particles were 3.26 nm and 1.76 nm when the molecular weights of linear polyethyleneimine were 25000 and 2150, respectively. These nanoparticles were well-dispersed in water in the range of pH 1 to 6. Branched polyethyleneimine also provided nanoparticles that dispersed in water in the range of pH 0 to 8. Linear poly(ethyleneimine-co-*N*-methylethyleneimine) gave nanoparticles that dispersed in water in the range of pH -1 to 15.

The reduction of bis(acetylacetonato)platinum(II), nickel(II) acetate tetrahydrate, and molybdenum(II) acetate dimer in a mixed solvent of oleylamine and diphenyl ether using 1,2-hexadecanediol resulted in the production of oleylamine-protected ternary alloy nanoparticles (NiMoPtNPs). Ligand exchange reaction with 50% *N*-methylated linear poly(ethyleneimine-*co*-*N*-methylethyleneimine) (poly(EI-*co*-NMEI)) in chloroform resulted in the production of poly(EI-*co*-NMEI)-protected NiMoPtNPs. The resultant nanoparticles had average diameters 1.9 to 2.5 nm and dispersed in water in the range of pH −1 to 14. The averaged radii of the NiMoPtNPs were decreased when the protecting polymer was changed from oleylamine to poly(EI-*co*-NMEI). Energy dispersive X-ray spectroscopy of poly(EI-*co*-NMEI)-protected NiMoPtNPs was performed to confirm the formation of polymer-protected alloy nanoparticles of nickel, molybdenum, and platinum.

1. INTRODUCTION

Platinum is known as a highly-durable and high-activity catalyst in both synthetic organic chemistry and environmental science and is widely used in these scientific areas. Platinum nanoparticles (PtNPs) are also used as an environmental catalyst for cleaning the exhaust gases from automobiles and factories.

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When the PtNPs are applied to a catalyst, they are often supported on the surface of silica or alumina gel. In recent years, platinum catalyst has been prepared by deposition on the surface of a mesoporous silica support which is formed in a honeycomb structure by the accumulation of long silica channels. The PtNP-supported mesoporous silica catalyst is prepared by two pathways. The first pathway consists of immersion of mesoporous silica in a solution of platinum nanoparticles. Alternatively, the first pathway can be performed by sol-gel reaction of alkoxysilanes in the presence of surfactant and PtNPs under an acidic condition to assist in the hydrolytic polycondensation of alkoxysilanes. In the second pathway, the preparation of mesoporous silica and the installation of PtNPs are performed in a parallel way, which means that the PtNPs are deposited on the silica surface during the formation of silica gel. Because such a sol-gel reaction is performed under an acidic condition, the PtNPs have to be stable under a low pH, such as a pH of less than 1. Polyvinylpyrrolidone-modified PtNPs are disadvantageous for the preparation of platinum-silica catalyst because of the low stability under an acidic condition to form a precipitation of platinum metal, which is not supported on the surface of silica gel. The low stability of polyvinylpyrrolidone-modified PtNPs is due to the low stability of the coordination of the pyrrolidone moiety to platinum under an acidic condition. For the preparation of such platinum nanoparticles, a chemical modifier stronger than polyvinylpyrrolidone is necessary. For example, chemical modification of platinum using the coordination of the nitrogen atom is one of the candidates for forming a stronger coordination bond with platinum compared with that formed by coordination with an oxygen atom.

In this work, therefore, nitrogen containing polymer chemical modifiers was selected for the preparation of PtNPs. Namely, the preparation of PtNPs using linear polyethyleneimine (LPEI), branched polyethyleneimine (BPEI), and a copolymer of ethyleneimine and N-methylethyleneimine (poly(EI-*co*-NMEI)) was studied.

2. PREPARATION OF NANOPARTICLES

We confirmed the preparation of PtNPs based on the color change of the solution from transparent to black as the duration of heating was increased. LPEI (M_W 25000)-protected PtNPs (No. 1) were obtained. Because the platinum content of PtNPs was measured by thermogravimetry analysis to be 14.7%, the percentage of the reactivity of hexachloroplatinic(IV) acid was calculated as 45.4%. The differential thermal analysis-thermogravimetry under air atmosphere showed a small endothermic peak around 300 ^oC and a big exothermic peak around 400 ^oC with weight losses, and the residue at 1000 ^oC was platinum. In the ultraviolet-visible absorption spectrum of LPEI (M_W 25000)-protected PtNPs in water, the absorption peak at 262 nm due to hexachloroplatinic(IV) acid disappeared, which supports the idea that platinum(IV) ion was reduced to platinum(0). The LPEI (M_W 25000)-protected PtNPs were mixed with hydrochloric acid or sodium hydroxide solution in order to observe the stability under various pH values. The nanoparticles were stable and well-dispersed in water in the range of pH 1 to 6.

On the other hand, LPEI (M_W 2150)-protected PtNPs (No. 2) were obtained. The content of platinum and the percentage of the reactivity of hexachloroplatinic(IV) acid were 18.1% and 84.4%, respectively. These nanoparticles were well-dispersed in methanol, ethanol, and water in the range of pH 1 to 6.

The average sizes of the nanoparticles were evaluated by measuring the diameter of nanoparticles in the TEM images. The average sizes of PtNPs No.1 and 2 were 3.26±0.45 nm and 1.76±0.52 nm, respectively. These data suggest that the diameter of PtNPs is dependent on the molecular weight of LPEI.

LPEI/BPEI-protected PtNPs were prepared by using LPEI and BPEI as protecting polymers, and the results of the preparation are summarized in Table 3. The mass ratio of LPEI and BPEI polymer, LPEI:BPEI, showed values of 5:5, 3:7, or 0:10. The LPEI/BPEI-protected PtNPs were obtained in 20.1 mg (No. 3), 13.6 mg (No. 4), and 9.1 mg (No. 5), while the platinum contents were 10.9% (No. 3), 28.2% (No. 4), and 27.9% (No. 5). The platinum yield was calculated as 20.5% (No. 3), 33.9% (No. 4), and 22.5% (No. 5). The LPEI/BPEI-protected PtNPs were a highly-viscous black liquid. These nanoparticles were dispersed in water in the range of pH 0 to 8, or pH 0 to 9. The secondary and tertiary nitrogen atoms in polyethyleneimine established the stronger coordination to the platinum atoms to increase the pH range of dispersion in water. In addition, the stable pH range for the dispersion of PtNPs could be controlled easily by modifying the amount of tertiary nitrogen atoms in the polyethyleneimine chain. The average sizes of LPEI/BPEI-protected PtNPs were 1.64±0.21 nm (No. 3), 3.09±0.72 nm (No. 4), 1.74±0.20 nm (No. 5).

In order to confirm the effect of the introduction of tertiary nitrogen atoms in the polyethyleneimine chain, some nitrogen atoms in LPEI were methylated by Eschweiler-Clarke reaction to give poly(EI-*co*-NMEI) with various degrees of methylation. In this reaction, the methyl group derived from formaldehyde is introduced to nitrogen atoms in polyethyleneimine in approximately quantitative yield, and the degree of methylation is controlled by the molar ratio of formaldehyde to the corresponding structural unit of ethyleneimine in polyethyleneimine. Based on this property, poly(EI-*co*-NMEI)-protected PtNPs with 17%, 40%, 56%, 88%, and 100% *N*-methylations were prepared and the results are summarized in Table 4. The poly(EI-*co*-NMEI)-protected PtNPs were obtained in 6.3 mg (No. 6), 8.6 mg (No. 7), and 4.5 mg (No. 8), while the platinum contents were 13.5% (No. 6), 9.8% (No. 7), and 10.6% (No. 8). The platinum yield was calculated as 15.2% (No. 6), 15.1% (No. 7), and 8.5% (No. 8). When the N-methylations were 17%, 40%, and 56% (No. 6 ~ 8), the poly(EI-co-NMEI)-protected PtNPs were a viscous brown liquid and dispersed in hydrochloric acid or sodium hydroxide solution in the range of pH -1 to 15. In contrast, when the N-methylations were 88% and 100% (No. 9 and 10), brown solids were obtained that showed no dispersion in water or various organic solvents. In contrast, a black precipitate of platinum was formed when these poly(EI-*co*-NMEI)-protected PtNPs were mixed with aqueous ammonia. The average sizes of poly(EI-*co*-NMEI)-protected PtNPs were 2.17±0.40 nm (No. 6), 2.38±0.43 nm (No. 7), 3.24±0.64 nm (No. 8). When percentage of *N*-methylations of poly(EI-*co*-NMEI) increased, sizes of PtNPs increased accordingly.

Oleylamine-protected NiMoPtNPs were prepared by a hot-soap method and obtained as a black powder. The initial molar ratio of nickel, molybdenum, and platinum, Ni:Mo:Pt, was set to 1:1:1 – 5:1:1 or 10:1:1. The nanoparticles contained no molybdenum when the molar ratio of nickel to molybdenum was higher than 5. This is because the reduction of nickel(II) species was accelerated due to the large content of nickel compound compared to that of molybdenum compound. The size of the nanoparticles was evaluated by measuring the diameter of the nanoparticles in the TEM images to be 2.1–6.8 nm, which increased with the increasing content of nickel.

Many methods for the ligand exchange of organically protected metal nanoparticles have been reported. For example, the exchange between a hydrophobic and a hydrophilic ligand using oleic acid-protected FePtNPs and 2-aminoethanethiol in methanol at room temperature for 10 min has been described. In this study, we conducted a ligand exchange from oleylamine-protected NiMoPtNPs to N-methylated poly(EI-*co*-NMEI) in water, methanol, ethanol, or chloroform with heating or ultrasonication. Ligand exchange was accomplished only in chloroform. We confirmed the ligand exchange of NiMoPtNPs by confirming their dispersion in ethanol after heating. As a result, poly(EI-*co*-NMEI)-protected NiMoPtNPs were obtained as a black viscous liquid.

The ligand was successfully exchanged to yield NiMoPtNPs as a black and viscous liquid. Compared with those of the oleylamine-protected NiMoPtNPs, these contents were lower, but oxidation was not observed. The metal molar ratios were measured by ICP analysis. The metal compositions were altered to some degree by the ligand exchange. No relationship was observed between the metal compositions of the oleylamine-protected NiMoPtNPs and the poly(EI-*co*-NMEI)-protected NiMoPtNPs, which suggests that nickel is oxidized more easily than molybdenum or platinum. The average sizes of these nanoparticles were smaller because some metal atoms were lost during the ligand exchange. These metal losses were also observed in the metal yields of the nanoparticles. The ligand exchange was affected by nickel because nickel is more easily oxidized than platinum, which resulted in the decomposition of nanoparticles during the ligand exchange. In other words, oleylamine-protected NiMoPtNPs with a nickel ratio over 63% failed to exchange the ligand.

EDS was carried out for a particle of alloy. The average composition was Ni:Mo:Pt = 9:29:62 in atomic ratio, which is relatively close to the composition of 9:16:75 determined by ICP. EDS mapping revealed that three metals were distributed uniformly in each particle. Metal atoms of Ni, Mo, and Pt were mixed uniformly to form a trimetallic random alloy.

The nanoparticles of trimetallic random alloy were mixed with hydrochloric acid or aqueous sodium hydroxide solution to observe their stability at various pH values. They were well dispersed in water over pH levels ranging from −1 to 14 immediately after mixing and were precipitated at pH 14 after standing for one week.

ACKNOWLEDGEMENT

This research was supported by CLUSTER (the second stage) of the Ministry of Education, Culture, Sports Science, and Technology, Japan and a Grant-in-Aid for Scientific Research on Innovative Areas “New Polymeric Materials Based on Element-Blocks (No. 2401)” (24102008A02) of The Ministry of Education, Culture, Sports, Science, and Technology, Japan.