Effective Electrochemical Activation of Oleate-Residue-Fouled Pt Nanoparticle Catalysts for Methanol and Formic Acid Oxidation

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ABSTRACT: Platinum plays a crucial role in the field of basic electrochemistry, regeneration energy, and so on. Pt nanomaterials with well-controlled size and shape could be easily obtained from metal–oleate complexes. However, these nanoparticles (NPs) could be electrochemically inactive because of the attached organic residue. This work has been reported as a robust method to remove the residues from the surface of Pt nanoparticle catalysts by the electrochemical treatment in alkaline media. After the electrochemical activation, the Pt nanoparticle catalysts showed good catalytic behavior toward the electrochemical oxidation of methanol and formic acid.

1. INTRODUCTION

For several decades, low-temperature fuel cells have attracted great interest from scientists and engineers in the field of alternative energy because of their simple system and high energy density. The ease of transport and stability at ambient conditions of fuel are additional advantages of low-temperature fuel cells. In the fuel cells, catalysts that are made of metal nanoparticles (NPs) and supporting materials for the electrochemical reaction are key components. Among various metal nanoparticles, Pt nanoparticles (NPs) have been the most extensively used materials in fuel oxidation and oxygen reduction reactions. PtNPs catalyst could be synthesized by various methods, such as impregnation, microemulsion, and electrodeposition in aqueous solutions with or without a surfactant. The synthesis of PtNPs in aqueous solutions was routinely used. However, it is relatively difficult to precisely control the size and shape of the NPs when compared with the organic solvent-based synthetic methods.

Through organic solvent-based synthetic methods, highly uniform nanoparticles, nanowires, and nanocubes could be synthesized from metal cationic precursors in the presence of oleate or stearate as a surfactant. There are already many reports on the synthesis of noble metal nanoparticles, such as Au, Pt, and Pt alloy nanomaterials, with well-controlled size and shape using metal–oleate complex. Pt and Pt alloy nanoparticles prepared from the Pt–oleate complex had very uniform size distribution, however, these NPs were electrochemically inactive because of the fouling of the attached organic residues. Several groups have made attempts to address this problem. Sun et al. have reported that grafted organic on the NPs were successfully removed by several hours of washing with acetic acid solution at 70 °C. Feliu and Zou groups reported that Pt nanoparticles and nanocubes could be washed by a mixture of hexane/ethanol. Heat treatment is also a routinely used method to remove attached organic molecules on the NPs. Somorjai et al. proposed the UV–ozone treatment method to remove capping agents using the UV–ozone chamber. Lee group introduced the ultrasonication process to remove the capping agent for 5 h. Recently, Solla-Gullo et al. reviewed the cleaning methodologies on the surface of metal nanoparticles. Although these methods are effective to remove organic residues, these processes are usually time-consuming and involve harsh conditions.

Herein, a new way for the removal of organic impurities on the surface of metal nanoparticles in the alkaline media is introduced. We propose a simple electrochemical method in alkaline solution to effectively remove the organic residues from the surface of Pt nanoparticles which were synthesized on the carbon substrate using the metal–oleate complex by simple
heat treatment. The electrochemical activity of the initially synthesized Pt catalysts was severely hampered due to the organic residues as formed from the degradation of the oleate chain during the synthesis. After the electrochemical treatment in alkaline media, the electrocatalytic behavior of these catalysts for methanol and formic acid oxidation was significantly recovered.

2. RESULTS AND DISCUSSION

For preparing Pt nanoparticles, we introduce the facile heat treatment method using Pt−oleate complex as the precursor. The Pt−oleate complex was obtained by simple mixing of Pt acetylacetonate and oleate solution. Then, the Pt−oleate complex was homogeneously mixed with carbon black by grinding. The mixture was then heated at 200 °C for 3 h under a N₂ atmosphere to form Pt/C catalyst. The Pt−oleate complex was converted into monodisperse Pt nanoparticles (PtNPs) on the surface of carbon black upon heating under the inert atmosphere. Simultaneously, the organic residue grafted the Pt nanoparticles through the thermal decomposition of oleate.

Figure 1A−C shows high-resolution transmission electron microscopy (HR-TEM) and high-angle annular dark-field (HAADF) images of 2 nm PtNPs obtained from the synthesis. These composites were washed several times using hexane and ethanol and then dried in a vacuum oven to remove oleate residues. Each PtNP had a highly crystalline structure with d-spacing of 0.23 nm, which is in agreement with the (111) lattice parameter of the face-centered cubic structure of Pt. The crystalline structure of Pt was confirmed by the X-ray diffraction (XRD) pattern of Pt (JCPDS 4-802) (Figure 1D) and the average NP size was calculated to be 2.3 nm by the Debye−Scherrer equation.

The catalytic activity of the PtNPs toward methanol and formic acid oxidation was studied and estimated using an electrochemical system. The initial cyclic voltammograms (CVs) of the catalyst were obtained before activation and showed weak hydrogen adsorption and desorption peaks due to grafted organic residue, as shown in Figure 2A. According to Somorjai et al., it was reported that

![Graph showing cyclic voltammograms before and after a recovery cycle of Pt/KB](image link)

Figure 2. Cyclic voltammograms before and after a recovery cycle of Pt/KB (A) in 0.5 M HClO₄, (B) in the mixture of 0.5 M CH₃OH and 0.5 M HClO₄ in comparison with commercial Pt/C (20 wt %, Tanaka), and (C) in the mixture of 0.5 M HCOOH and 0.5 M HClO₄.
were barely observed during the first scan, which means that the surfaces of PtNPs were contaminated by organic residues.\textsuperscript{23} Interestingly, the peak intensities of hydrogen adsorption/desorption and the reduction of Pt oxide were raised in increments with each cycle, and the peaks reached their diffusion-limited maxima at 15 cycles, at which point the inactive sites on the surface of the catalysts were converted to active sites. Hydrogen adsorption/desorption peaks are fully recovered in the cyclic voltammetry test after 15 cycles, which means that the recovery reaction terminates after 15 cycles. It is important to confirm the termination reaction in terms of checking hydrogen adsorption/desorption peaks instead of counting cyclic numbers. In Figure 4, the morphology of Pt nanoparticles in electrochemical treatment to remove organic shells is represented. The images show that there is no effect and change in morphologies before and after treatment, and the d-spacing of these nanoparticles before and after treatment were calculated to be 2.267 and 2.258 Å, respectively. This phenomenon explains that this method makes organic shell removal not successful to Pt nanoparticles. We proposed the mechanism of cleaning using the electrochemical process in alkaline solution in Figure 5. The key factor for successful deactivation of metal nanoparticles is electrochemical activation in alkaline solution. Oleylamine is widely used in solvothermal metal or metal oxide nanoparticle synthesis owing to its high boiling point and its role as a mild reducing agent and is a co-surfactant with oleic acid. Even though oleylamine acts as a co-surfactant with oleic acid, the charge repulsion with metal precursor occurs in the mixing solution. Oleic acid plays the main role of surfactant and oleylamine as the stabilized solution in the surroundings of capped metal nanoparticles and reducing agent.\textsuperscript{26–28} Organic-capped Pt nanoparticles show that the equilibrium of net charge between metal NPs and surfactant was stabilized. However, outer layer organics are detrimental to the electrocatalytic reaction. The residual organic on PtNPs have to be removed by electrochemical polishing to activate the PtNP catalyst in the fuel oxidation reaction.\textsuperscript{29} To solve this problem, the charge balance of organic-grafted Pt nanoparticle has to be broken by the applied negative potential and Pt metal nanoparticles were decontaminated in KOH, which means that oleylamine and oleic acid have ethylene double bonds in the chain. In the saponification reaction, an alkaline gradient, such as NaOH and KOH, is widely used to remove surfactant and organic residues.\textsuperscript{30} KOH, serving as a source of OH\textsuperscript{−} as a nucleophile in organic chemistry, attacks adsorption bonding between metal NPs and the organic residue and the applied potential accelerates to strip off the organic residue. These organic residues on the surface of metal are effectively eliminated in the alkaline condition. Therefore, the cleaning effect of organic-grafted metal nanoparticles might be effectively accelerated by these phenomena.

To further study, we examined the catalytic performance of the PtNPs for the electrooxidation of methanol using an electrochemical analyzer (see the Experimental Section), and the results are shown in Figure 2B. The commercial Pt/C catalyst in Tanaka was introduced to compare with the as-synthesized catalyst. After alkaline treatment, the Pt/C catalyst showed peak potentials of +0.6 and +0.8 V in the cathodic and anodic scans, respectively, in the presence of 0.5 M methanol. The oxidation peak of methanol was not observed before treatment, which could be explained by the fact that the organic residue on the Pt surface blocked access to the electrocatalytically active sites before the activation treatment. The electrocatalytic activity was definitely recovered by electrochemical scanning in an alkaline solution since the organic residue is removed from the Pt surface. Interestingly, this treatment only worked in alkaline media (as opposed to acidic media). We also observed these phenomena during the oxidation of formic acid (Figure 2C). PtNPs prepared by the Pt−oleate complex precursor could be applied to the electrooxidation of both methanol and formic acid. Different PtNP weight % of Pt/C catalysts were applied as electrocatalysts for the oxidation of fuel in Figure 6. The electrocatalytic properties of 12 wt % Pt/KB are analogous...
to those of 40 wt % Pt/KB. The electrocatalytic activity of these catalysts was activated and recovered by electrochemical treatment for methanol and formic acid oxidation as seen in Figure 6. To confirm the scalability, 12 and 40 wt % Pt/KB catalysts were calculated in mass activity. The mass activities of 12 and 40 wt % Pt/KB catalysts are almost equal, 2.083 and 2.215 mA/g/cm², respectively.

3. CONCLUSIONS
We demonstrated that the inactive PtNPs prepared by Pt−oleic acid and oleylamine complex precursor could be recovered and activated by electrochemical treatment in alkaline solution to easily remove organic residue from the surface of metal nanoparticles. The electrochemically treated Pt nanoparticles exhibited excellent catalytic performance for methanol and formic acid oxidation. This method could provide a general approach for electrochemical activation in alkaline media of inactive contaminated catalyst by oleic acid and oleylamine.

4. EXPERIMENTAL SECTION

4.1. Materials. Oleylamine (OAm, >70%) and oleic acid (OA, >70%) were purchased from Samjung company. Pt(acac)_2 and RuCl_3 were purchased from Aldrich. The deionized (DI) water was used from a Millipore Auto system. All of the reagents were of analytical grade and used without purification.

4.2. Synthesis and Characterization of Pt−Oleate Complex. In a typical synthesis, preparation of Pt−oleate complex, 0.038 g of platinum acetylacetonate (Pt(acac)_2, 0.1 mmol, Sigma-Aldrich, 98%) was dispersed in 0.5 mL of oleylamine and 0.5 mL of oleic acid. And then 0.1 g of Ketjen Black EC-300J (Ketjen Black International Company) was mixed with the Pt−oleate complex by simple grinding with a pestle and mortar. The mixture of Pt−oleate and ketjen black was heated at the heating rate of 5 °C/min under a nitrogen atmosphere and then kept at 200 °C for 3 h. Transmission electron microscopy (TEM) and HAADF-STEM images were conducted using a JEOL EM-2100F microscope. X-ray diffraction (XRD) characterization was carried out using Rigaku Dmax 2500 diffractometer.

4.3. Electrochemical Measurements. The electrochemical measurements of methanol and formic acid oxidation were conducted with an electrochemical analyzer (Autolab PGSTAT302N) with a 5 mm diameter glassy carbon electrode (GCE) as the substrate/working electrode and a platinum wire as the counter electrode. Ag/AgCl (Bioanalytical Systems, Inc.) and Hg/HgO as reference electrodes were used in acidic and alkaline conditions, respectively. The working electrode was modified in the following manner: 10 mg of catalysts (Pt/KB), 300 μL of isopropyl alcohol (IPA), and 100 μL of Nafion solution (Sigma-Aldrich, 5 wt % Nafion in DI water) were dispersed in 500 μL of DI water. The slurry ink was ultrasonicated for 20 min. Slurry ink (8 μL) was dropped onto the GCE and dried using an IR lamp. The test solution was 0.5 M of HClO_4. The catalysts were cycled at a scan rate of 100 mV/s at room temperature until stable cyclic voltammograms (CVs) were obtained. The activation process was performed in 0.5 M of KOH solution while purging with nitrogen and cycled at a scan rate of 100 mV/s at room temperature. After activation, the treated sample was measured.
in solutions of 0.5 M of HClO₄ + 0.5 M methanol and 0.5 M of HClO₄ + 0.5 M formic acid.

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