

Uniformly Distributed Metal Nanoparticles in Various Sized Porous Catalytic Supports by NPP Process

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ABSTRACT

Noble metal nanoparticles such as Pt and Pd were fabricated on glucose (Gl) powder by using physical vapor deposition, so called nanoparticles on powder (NPP) process. The precious metal nanoparticles were loaded on the surface of porous support such as activated carbon (AC) or monolith ceramic. The Pd/AC catalysts were fabricated by NPP process and their characteristic chemical reaction compared with commercial 5% Pd/AC. The catalytic property of the catalyst was estimated from the chemical reaction of hydrogenation of acetophenone (AP). The catalyst by NPP process showed higher performance in terms of reaction activity and selectivity compared to pre-existed commercial one. In case commercial Pd/AC, most of Pd nano particles were aggregated each other on the surface of AC support. The higher catalytic performance of the NPP processed catalyst induced from uniform distribution of small sized nano particles with low agglomeration between nano particles each other on the surface of the AC support. And also Pd and Pt nano particles on the surface of the monolith were observed by SEM. The distribution of metal nano particles on the porous support was observed by electron microscope such as SEM and TEM. The size of the Pt and Pd nanoparticles on the powder by NPP process was 2~3 nm and 3~5 nm, respectively.

Keywords: nanoparticle, catalyst, support, porous, activated carbon, ceramic monolith

1 INTRODUCTION

Catalyst from noble metal to transition metal or their oxide plays a very important role in reducing activation energy in various key chemical reactions. Catalysis is suggesting a clue to 'green chemistry' with reducing consumption of raw materials, eliminating toxic or waste by-products, saving input energy of industrial processes, etc [1-3]. Various formation methods of industrial heterogeneous catalysts have been suggested not only chemical reduction process from metal salts uniform nano sized particles (<10 nm in size) distribution on support but also direct loading nanoparticles in colloid state. But agglomeration or accumulation of the nanoparticles during the process have resulted in reduction of catalytic efficiency and overuse of the catalyst materials [4-10]. In fabrication

process of catalyst using nanoparticles of novel metal, main task is solving aggregation or agglomeration of nanoparticles. In order to solve that problem and increase catalytic efficiency, we have made nanoparticles by NPP process and fabricated various catalysts with porous supports such as AC or monolith. Environment friendly and physical NPP process shows easy approach to various application such as anti-microbial fiber, catalytic converter, functional plastics, catalysts for fine chemicals, agricultural products, etc. This article introduces new catalyst by NPP process which shows well distribution of the nanoparticles on porous supports such as AC or monolith and higher performance of that.

2 EXPERIMENT

The precious metal nano particles such as Pt or Pd are formed on the powdery glucose support by NPP process as shown in Fig. 1. The nano particles are generated from the target material by DC magnetron sputtering. In NPP process, the sputtered particles from the target are arrived and attached on the surface of powdery support material during mixing the supports in barrel. The nano particles are firstly formed on the surface of the support by exposure to the sputtering zone, and the support with nano particles hides abruptly into the powdery supports in the barrel. New nano particles are formed on the surface of the support whenever the support is exposure to the sputtering zone. Exposure time of the support to the sputtering zone is sufficiently short compared to the travelling time of that in the barrel. The nano particles content on support can be controlled by sputtering time. The sputtering power and vacuum degree is 500 W and 5×10^{-4} Torr during NPP process respectively. The content of Pt nano particles in the Pt/Gl powder is 3,000 ppm and that of Pd in Pd/Gl also 3,000 ppm. The content was measured by inductively coupled plasma (ICP) method.

Catalysts with porous support such as AC or monolith were fabricated by post process using 3,000 ppm Pd/Gl or Pt/Gl powder.

For making Pd/AC catalyst, the mixture of the Pd/Glucose, AC, and deionized water (DIW) was stirred at room temperature during 2 hrs in an ultrasonic bath. The temperature of the solution was about 35°C after 2 hrs. Water and glucose were removed from the mixture by filtering process with filter paper. The Pd/Gl sample was washed with 70°C hot water. 2% and 5% Pd/AC catalyst were fabricated for the comparison with commercial 5%

Pd/AC. NPP processed Pd/AC and purchased commercial Pd/AC were dried at temperature of 110°C during 10 hrs in vacuum chamber before chemical reaction experiment. The Pd quantity in the catalyst after dry was also measured by ICP.

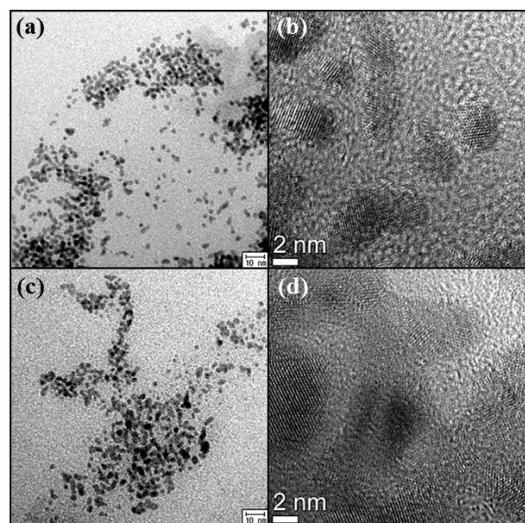


Figure 1: TEM images of Pt (a, b) and Pd (c, d) nanoparticles by NPP process.

AP as a reactant was used for the standard chemical reaction of the Pd/AC catalyst. The Pd/AC catalyst (0.23 g), AP (6 g), and ethanol (20 g) were inserted in reactor and hydrogen gas was charged up to 2 MPa in the reactor. The volume of the reactor was 100 mL. The reactant with catalyst was stirred with agitator and the temperature of the reactor was held at RT during the experiment. After finishing the reaction, the solution was taken from the reactor. The catalyst and chemical solution were separated by centrifuge. Ingredient of the chemical solution was analyzed by gas chromatograph (GC) method. The reactivity and selectivity of the AP depending on the Pd/AC catalysts were estimated from the GC experiment result.

Precious nano metal was loaded on ceramic monolith by post process with NPP processed powder. Colloidal solution including precious metal such as Pd or Pt was synthesized by dissolving glucoses of Pd/Gl or Pt/Gl powder in water. The metal nano particles were well dispersed in water, and the content of the metal in the solution was 1,000 ppm. In order to load nanoparticles on the surface of monolith, cylindrical ceramic monolith (9 cm in diameter, 5 cm high) was dipped in the colloidal solution. Ultrasonic wave was applied to improve the loading distribution of nanoparticles in the complicated structures of monolith during dipping monolith in the solution. The monolith containing metal nanoparticles was dried for 12 hrs at room temperature after dipping for 3 hrs. In order to improve adhesion between nanoparticles and the substrate

and improve high temperature stability of the nanoparticles, the monolith was heated at 600°C for 6 hrs.

The nanoparticles distribution of the samples such as Pd/AC, Pd/monolith, and Pt/monolith were investigated by FE-SEM and ICP-AES.

3 DISCUSSION

The 2%, 5% Pd/AC catalysts and commercial 5% Pd/AC catalyst with the weight of 0.23 g were tested at the same chemical reaction condition, respectively. As shown in Fig.2, the AP conversion using the 2% Pd/AC catalyst is 21% after reaction time of 0.5 hr while the commercial one is 24%, and that of the 2% Pd/AC is 87.5% and commercial terminated after 2 hrs. Catalytic activities of the 5% Pd/AC catalyst fabricated in three different batches are nearly the same as shown in Fig. 2 (b), which means the Pd/AC catalysts have a good reproducibility. The AP reaction of the 5% Pd/AC and commercial is terminated at 1.17 hr and 2 hrs, respectively. The reaction time of the 5% Pd/AC was nearly two times faster than that of commercial one.

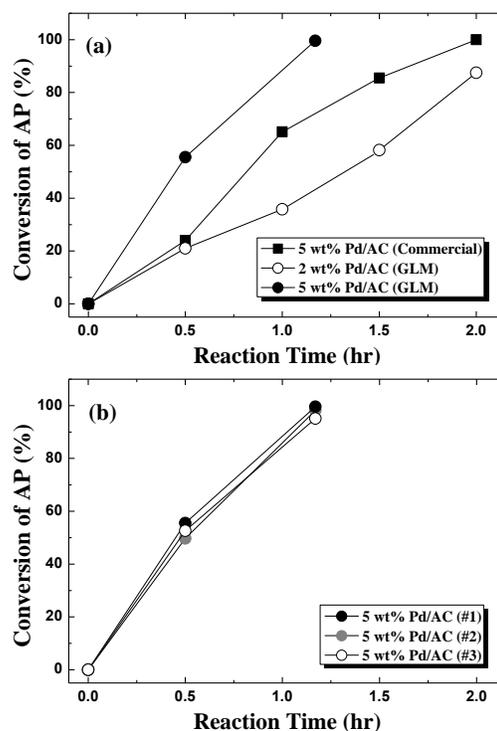


Figure 2: Conversion of the AP with (a) 2%, 5% Pd/AC vs. commercial 5% Pd/AC, (b) three different samples of 5% Pd/AC.

The SEM images of the commercial vs. the Pd/AC catalysts are observed. It is clearly shown that the Pd nano particles of the catalyst (small white dots) are much more uniformly distributed on the AC than that of the commercial one. Agglomerated large size of Pd particles (several hundreds of nano meters) are clearly shown on the

commercial catalyst as shown in Fig. 3 (a) and (b), but not shown them on the catalysts in Fig. 3 (c) and (d). The TEM images are observed on the surface of the commercial 5% Pd/AC, the NPP processed 2% Pd/AC and 5% Pd/AC as shown in Fig. 4 (a), 4 (b), and 4 (c), respectively. Even though the TEM image of the commercial catalyst in Fig. 4 (a) shows uniform distribution of the nano particles on the AC surface, most of the Pd particles are micron size as shown in Fig. 3 (a) and (b). The size of the Pd nano particles of the 2% and 5% Pd/AC catalysts are <10 nm (mainly 2-5 nm size). And the NPP processed neutral Pd nano particles are uniformly sit on the AC support without agglomeration even at the high concentration of 5%.

SEM images on the surface of the monolith were shown in Fig. 5. There are three types of agglomerated nanoparticles such as ~50 nm sized islands (Fig. 5d), linked large sized island (Fig 5c, 5f), and ~100 nm sized porous film shape (Fig. 5a, 5b and 5e). Agglomerated Pt particle was smaller than Pd or Pt+Pd particle in the monolith. As the SEM images were obtained from the dark points whose area is less than 1% compared to whole surface of the monolith, the size of most metal nanoparticles in the monolith should be 2 ~ 10 nm as shown in Fig. 1.

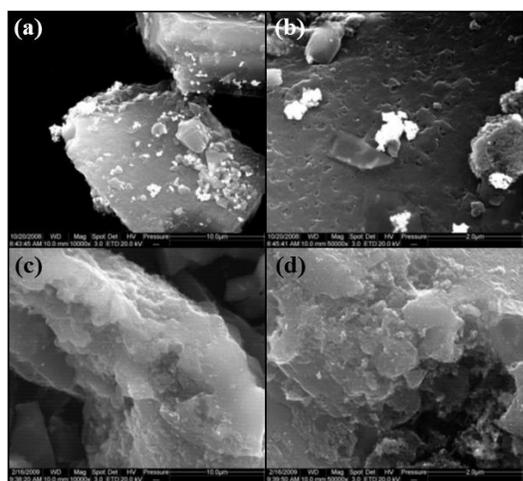


Figure 3: The SEM images of commercial 5% Pd/AC (a, b) and NPP processed 2% Pd/AC (c, d).

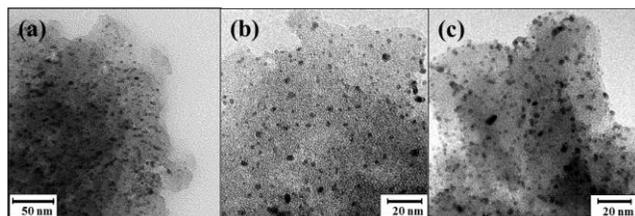


Figure 4: The TEM images of commercial 5% Pd/AC (a) and NPP processed 2% Pd/AC (b) and 5% Pd/AC (c)

The coarsened metal particles was not serious in heat treatment because the size of the particles was below 50 nm. The fine and porous structured nanoparticles would not have an effect on the air flow through the monolith air channel. In chemical process of catalytic converter, the ionic molecules such as PtCl_6^{2-} , H^+ with water flow out through micro porous capillary channel from the inside of ceramics to outside wall during dry process. The PtCl_6^{2-} , H^+ and water on outer surface of monolith are recrystallized to H_2PtCl_6 with water vaporizing. The decomposition of metal salt at the surface by high temperature results egg shell shape, egg white, egg york shape distribution of Pt nanoparticles formation in the monolith. This is the main problem of the chemical processed catalytic converter because of low catalytic performance and overuse of novel metal.

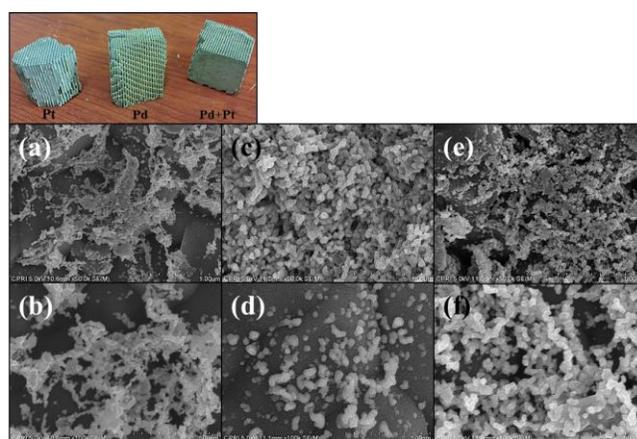


Figure 5: The photo and SEM images of Pt (a, b), Pd (c, d), and Pt+Pd (e, f) nanoparticles on the surface of the monolith ceramic.

On the other hand, the catalytic converter with using NPP processed precious nano metal shows well distribution of nano particles on the monolith surface. The colloidal solutions are easily flowed and filled into the air flow channel and porous channel of the monolith. The metal nanoparticles move and stick on inner surface of the monolith during dry process while water and glucose moves to outer surface of that through the micro porous capillary channel. The nanoparticles are uniformly distributed on whole surface of the complicated structured monolith ceramic with appearing uniform color as shown in Fig. 5.

Figure 6 shows a schematic diagram of the metal nanoparticle formation on porous support such as AC or monolith with conventional chemical process and NPP process in Fig. 6 (a) and Fig. 6 (b), respectively. If porous support is dipped in metal salt solution containing various chemical agents such as reductant, dispersant, and PH control agent, the Pd^+ ion changes into Pd^0 neutral atoms on the surface of the porous support. Subsequently, large sized agglomerates are constructed on the surface of the porous

support by the interaction between continuously provided the Pd^+ ion and nucleation site of Pd^0 on the porous surface as shown in Fig 6 (a). Under the reaction of surfactant, the charged ions assemble to nucleation and grow up abruptly because the interaction between Pd^+ and Pd^0 by charge transformation is much stronger than that between Pd^+ and the surface of the porous support.

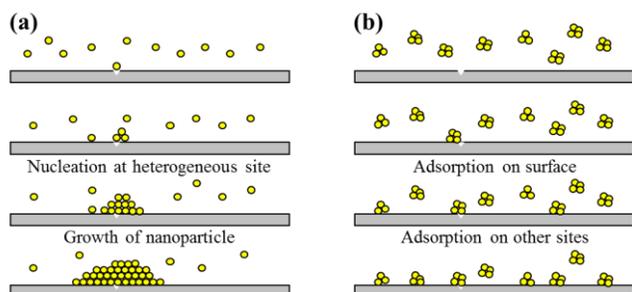


Figure 6: Schematic diagram of the nucleation of ionic metal particles (a) and the adsorption of the neutral metal particles (b) on the porous substrate.

On the other hand, the NPP processed Pd/AC, Pd/monolith, and Pt/monolith catalysts were prepared by physical method without charged metal ions and dispersion agents. As shown in the Fig. 3 (c), (d) and Fig. 5, metal nano particles can be easily absorbed on the surface of the porous support because the interaction between nano sized metal particles and the surface of the porous support is much stronger than that between metal nano particles each other. Those strong interaction and large surface area of the porous support result in uniform nano particles distribution on the surface of the porous support as shown in Fig. 6 (b).

4 CONCLUSIONS

The catalysts of precious metal on porous support were fabricated with neutral metal nano particles fabricated by physical NPP process. The catalytic performance of the Pd/AC catalyst by NPP process appeared higher than that of commercial one by chemical process. From the surface analysis of the catalyst, the Pd nano particles by NPP process were well dispersed on whole surface of AC support while that by chemical process were highly agglomerated on the AC surface. The large metal particles by chemical process resulting in lower catalytic performance were induced from the interaction between ionic metal particles and nuclei on the porous support. But well dispersed small metal nano particles by NPP process showed higher catalytic performance. Uniformly well distributed small metal nano particles on porous support resulting in larger surface area showed higher performance of the catalyst than that of commercial one. As a result, the NPP processed catalyst can be used in various application fields with simple fabrication process, saving material cost, various supports, alloy catalyst, and so on.

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