Preparation of Ordered Macroporous Platinum Metal Particles*

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Platinum metal particles having periodic macropores were prepared from close-packed silica spheres and an aqueous solution of hexachloroplatinum (IV) acid. The sizes of platinum macropores were controlled by the size of the silica spheres. [DOI: 10.1380/ejssnt.2006.451]

Keywords: Scanning electron microscopy; Surface morphology; Platinum spheres.

I. INTRODUCTION

Macroporous materials having bicontinuous and periodic voids of submicron order are expected to have significant applications in photonic crystals [1–3], electrodes [4], catalysts [5] and bioactive materials [6]. Especially, ordered macroporous metal particles are explored as materials for electrodes because they can be easily molded and have larger surface area values than those of flat metal plates and the bicontinuous macropores can promote mass transfer of large molecules to active metal sites. Control of the chemical composition and sizes of the macropores is a very important parameter in their application. Inorganic macroporous metal oxide materials can be prepared with a template method. After an infiltration of the solution of metal precursor into the interstice of colloidal crystals composed of organic polymer spheres followed by the removal of the polymer by calcination, metal oxide particles with periodic voids were obtained [1]. However, use of organic polymers as templates has several disadvantages such as i) if a shrinkage of the polymer templates during calcination occurred, then the size of voids in metal oxide particles could become smaller than those of the polymer spheres [7, 8] and ii) a residue of carbonaceous materials from the polymer templates after calcination remaining in the macroporous material could cause the blockage of pores leading to decrease the pore volume and surface area values [9]. The use of silica sphere arrays as templates and their removal by hydrofluoric acid would overcome the problems described above. It has been reported that the metal particles having ordered macropores could be prepared by the combination of the colloidal silica template and reduction with electro- or electroless plating methods [10, 11]. However, the plating methods require electrodes or metal nanoparticle as a starting point for reduction, which caused the contamination of the macroporous material. In this paper, we report the preparation of ordered-macroporous platinum metal particles with the combination of the silica template and conventional hydrogen reduction methods. We also report the control of the sizes of macropores by changing the sizes of silica spheres.

II. EXPERIMENTAL

All chemicals were purchased from Wako Pure Chemical Industries, Ltd. and used as received. Silica spheres were obtained by adding an ethanol-water solution of basic catalysts to an ethanol solution of tetraethylorthosilicate under stirring at 308 K [12, 13]. After washing with ethanol, the silica spheres were sedimentated and dried at room temperature, and then an opaque colloidal crystal of the silica spheres were obtained. The colloidal crystal was immersed into an aqueous solution of hydrogen hexachloroplatinate (IV) hexahydrate in the colloidal crystals. The solvent was removed by vacuum-drying at room temperature and a yellow platinum-silica complex was obtained. After reduction of the platinum-silica complex under flowing hydrogen at 573 K followed by hydrofluoric acid treatment, the final black platinum metal particles were obtained.

III. RESULTS AND DISCUSSION

SEM images of the colloidal crystals of silica spheres prepared with ammonia and methylamine catalysts are shown in Fig. 1. These spheres were well-ordered with (111) plane of face-centered cubic structure for both samples [14–16]. The sizes of silica spheres (the distance between the centers of adjacent spheres) prepared using ammonia and methylamine were 520 and 260 nm, and the surface area values were 7.6 and 15.8 m² g⁻¹, respectively. Surface area values were roughly corresponding to the calculated ones (6.1 and 12.2 m² g⁻¹) based on the diameters (520 and 260 nm) and the density of silica spheres (1.87 g cm⁻³) [17]. SEM images and the surface area values indicate that silica spheres were nonporous.

Low magnification SEM images of platinum metal are shown in Fig. 2. We confirmed that only characteristic X-ray of platinum was detected in the platinum metal particles after hydrofluoric acid treatment by EDX analysis. The surfaces of colloidal crystal were flat (not shown); however, those of platinum metal particles were rough, which would be formed by shrinkage of volume from hydrogen hexachloroplatinate (IV) to metal during hydrogen reduction. Figure 3 shows high magnification SEM images of the platinum particles. Well-ordered voids were...
FIG. 1: SEM images of the colloidal crystals of silica spheres; prepared with (A) an ammonia and (B) a methylamine catalyst.

FIG. 2: Low magnification SEM images of platinum metal particle. Silica spheres were prepared with (A) an ammonia and (B) a methylamine catalyst.

FIG. 3: A high magnification SEM image of the platinum particles. Silica spheres were prepared with (A) an ammonia and (B) a methylamine catalyst.

found to be arranged on the platinum metal particles. Distances between the centers of voids corresponded to those of the silica spheres used, indicating that colloidal silica crystals worked as template of macropores of metal particle. Figure 3 also showed dark images under the voids of the surfaces (shown in dotted). The images show interconnection (windows) between adjacent second layer’s voids, indicating the periodicity of voids. Surface area values of the platinum metal particles prepared with silica spheres of 520 and 260 nm were 2.7 and 4.1 m$^2$ g$^{-1}$, respectively and micro- and mesopores were not observed. These results indicate that platinum metal particles prepared from colloidal silica crystal templates are macroporous.

IV. CONCLUSION

Pure platinum metal particles having periodic macropores were prepared with the combination of template and hydrogen reduction methods.
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