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Fabrication of Microporous TiO_2 Using Two-step Replication of Fine Structure of Porous Glass

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TiO_2 with a textured porous structure was fabricated by two-step replication of a fine structure of porous glass. After making a negative type of porous glass with polymethyl methacrylate, porous TiO_2 were formed using a sol-gel process. This process resulted in textured porous TiO_2 with a geometrical structure identical to that of the starting porous glass.

Key Words : TiO_2 , Porous Glass, Replication, Sol-gel Process

1 Introduction

TiO_2 has been considered to be one of the most promising materials in various fields, including those related to photoanodes, photocatalysts, and sensors.^{1–5)} To optimize the efficiency of these devices, much effort has been made to preparing TiO_2 films with a textured surface of controlled morphology. However, the methods previously reported have not been satisfactory in terms of the homogeneity and range of producible pore size.^{3,4)} In the present report, we discuss a new process for preparing textured porous TiO_2 using porous glass as a template for the replication processes, and study the geometrical changes in their porous structure during the fabrication process and heat treatment.

Porous glass, which is produced by phase separation of two-component-system glasses by spinodal decomposition followed by selective dissolution of one component, has received considerable attention as a useful inorganic material because of the uniform distribution of pore size and chemical and mechanical stability.^{6–13)}

Using porous glass as a starting structure of the two-step replication process, we previously reported on the fabrication of a porous metal [Ni, Pt].¹⁴⁾ In this case, we confirmed that the geometrical structure of a porous glass with the pore size of 15 nm can be replicated exactly. We have continued our study of the two-step replication using porous glass and obtained TiO_2 with a textured morphology. Until now no work has been reported on the fabrication of a porous metal oxide using the fine structure of the porous glass as a template.

2 Experimental

Figure 1 shows an outline of the production process for porous TiO_2 . In this process, a negative porous glass matrix is produced using polymethyl methacrylate (PMMA), and the PMMA negative matrix is

filled with TiO_2 sol produced by hydrolysis of an alkoxide. After the TiO_2 sol is dried, the negative PMMA matrix is dissolved by acetone, and a TiO_2 porous structure with a geometry identical to that of the mother matrix is obtained.

The porous glass used as a matrix was provided by Ise Chemicals Co., Ltd (Tokyo, Japan). The sample is a plate ($5 \times 5 \times 0.5$ mm) having pores with an average size of 1 μm and an average volume of $0.42 \times 10^{-3} \text{ lg}^{-1}$.

First, the matrix was submerged in H_2O_2 (30 mass %) for 2 h for removal of organic substances adsorbed on its surface. Second, the sample was filled with methyl methacrylate monomer containing 5 mass %

Fig. 1 Schematic diagram of the fabrication process of microporous TiO_2 : (a) porous glass (mother template), (b) injection and polymerization of PMMA, (c) selective dissolution of glass (replicated negatype), (d) injection and drying of titanium alkoxide, (e) dissolution of PMMA (microporous TiO_2).

benzoyl peroxide. Third, the monomer was polymerized at 40 °C for 4 h. Next, the sample was placed in a HF solution (20 mass %) for selective removal of the glass phase. The interstitial space in the PMMA negative matrix was filled with a TiO_2 sol produced by the hydrolysis of $\text{Ti}(\text{O}-i\text{-C}_3\text{H}_7)_4$. The TiO_2 sol was prepared by a method similar to that reported by Kamiya *et al.*^{15,16} Then the TiO_2 sol was dried and solidified. Finally, the PMMA was removed with acetone. The porous TiO_2 gel was heated in a muffle furnace and was crystallized at 500 °C for 30 min and 1000 °C for 30 min in air. The surface of the sample after each production step was observed under a scanning electron microscope (SEM: JEOL JSM-6100). For the SEM observation, each sample was coated by Au sputtering for 3 min to avoid the charge up effect.

3 Results and Discussion

Figure 2 shows SEM images of the surface of the porous glass (Fig. 2a), negative porous glass matrix made of PMMA (Fig. 2b) and the final product of porous TiO_2 gel (Fig. 2c). In Fig. 2b, it is found that the reversed structure of the porous glass matrix was reproduced as the PMMA negative matrix. Based on this observation, we confirmed that the microstructure of the porous glass matrix was completely filled with PMMA. We also note that the PMMA negative matrix is adequately stable against the HF (20 mass %) solution used as an etching solution to remove the matrix of the porous glass. From Fig. 2c, it can be observed that the porous TiO_2 gel has the diameter of the pores in the matrix, similar to the geometry of the starting matrix.

It is known that TiO_2 gel prepared from alkoxide which is X-ray amorphous is crystallized to the

anatase phase at approximately 450 °C and takes on the rutile phase in addition to the anatase phase at 720 °C, and gives only the rutile phase at 1000 °C and above.^{15,16}

In this study, we heated TiO_2 gel at 500 °C and 1000 °C and observed a structural change of the gel by SEM. In the sample heated at 500 °C (Fig. 3), no change of the structure on the samples between before and after heat-treatment was observed, on comparing with Fig. 2c. On the other hand, structural changes were evident in the porous structure of the sample heated at 1000 °C, as shown in Fig. 4. Through the high-magnification SEM observation (Fig. 4b), we observed that the walls of the pores in the TiO_2 were composed of microparticles, and some of these particles grew to over 200 nm in size. However, the basic skeleton of the porous structure was maintained after heat treatment as shown in Figs. 4a and 4b.

Figure 5 shows X-ray diffraction patterns of postheated TiO_2 . In the TiO_2 gel heat treated below 200 °C, no distinct peak was observed in the X-ray pattern. However, the TiO_2 gel was crystallized to the anatase phase after heat treatment at 500 °C for 30 min, and to the rutile phase after the heat treatment at 1000 °C for 30 min. Based on these results, it was concluded that the porous TiO_2 was composed of anatase phase after the heat treatment at 500 °C for 30 min, and was transformed to the rutile phase after the heat treatment at 1000 °C for 30 min. Therefore, the small

Fig. 2 SEM micrographs of porous glass (a), replicated negative type with PMMA (b), and replicated positive type with TiO_2 (c).

Fig. 3 SEM micrograph of microporous TiO_2 after postheat treatment at 500 °C for 30min.

Fig. 4 SEM micrographs of microporous TiO_2 at 1000 °C for 30 min, low magnification (a) and high magnification (b) view.

Fig. 5 X-ray diffraction patterns of TiO_2 gel powder heat treated at different temperature. Peaks "A" correspond to the anatase phase and peaks "R" correspond to the rutile phase.

particles observed in porous TiO_2 heat treated at 1000 °C for 30 min were considered to be composed of the microcrystals of the rutile phase.

4 Conclusion

From the results shown in the present study, we draw the following conclusions: 1) fabrication of porous TiO_2 with a pore structure identical to that of porous glass is possible by a two-step replication process, and 2) the pore structure replicated using TiO_2 can be maintained after heat treatment at 1000 °C.

Porous TiO_2 produced by the method described here contains pores with homogeneous diameters and large surface areas. Furthermore, this method can be used

for production of porous materials of metal oxides other than TiO_2 , and is expected to contribute to a wide range of applications.

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