

Building Block Approach to SiO₂-TiO₂ Porous Materials

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(2-Hydroxyethyl)trimethylammonium silicate and titanium bis(triethanolamine) were allowed for a reaction in methanol. The reaction proceeded without breakdown of the Si₈O₂₀⁸⁻ structure of the silicate to give SiO₂-TiO₂ gels. Heat-treatment of the gels at 650-1000 °C in air for 1 h yielded SiO₂-TiO₂ powders with high surface areas (496-127 m² g⁻¹, respectively), whose TiO₂ component is dominantly present as anatase.

Thermal and chemical stability of high surface area materials is the major concern for their applications at elevated temperatures. It was demonstrated that thermally stable porous materials could be obtained in the B-N,¹ Si-C-O,^{2,3} SiO₂-TiO₂,^{4,5} and SiO₂-ZrO₂⁶⁻⁸ systems. The substances in the SiO₂-TiO₂ system^{4,5} were produced by leaching Al₂O₃-B₂O₃-CaO-MgO (or -Na₂O) out of phase-separated glasses in the SiO₂-TiO₂-Al₂O₃-B₂O₃-CaO-MgO (or -Na₂O) system. The glass-ceramics showed high durability as well and a small amount of the TiO₂ component was present as anatase even after heat-treatment at high temperatures where the transformation of anatase to rutile usually takes place, although rutile was the main phase of the TiO₂ component. The presence of anatase is a desirable feature for their use as the photocatalyst, since anatase has higher photocatalytic activity than rutile upon UV irradiation.

The building block approach has been shown to be one of procedures effective for synthesizing porous materials. In the procedure, compounds with the cage-like structure, such as the cubeoctameric silicate anion (Si₈O₂₀⁸⁻),⁹ are generally used as the starting material and reactions are carried out so that the compounds are linked without breakdown of the structure to form networks. The porous materials produced by the procedure demonstrated to have higher surface areas than those prepared using tetraalkoxysilane as a SiO₂ source,^{8,10} even if organic quaternary ammonium ions, used as organic templates in zeolite synthesis, are present in the reaction system.⁸

Consequently, this study has been aimed at synthesizing SiO₂-TiO₂ porous substances by the building block approach using the (2-hydroxyethyl)trimethylammonium silicate, Si₈O₂₀[N(CH₃)₃(C₂H₄OH)]₈·nH₂O, as a SiO₂ source and a 80% 2-propanol solution of titanium bis(triethanolamine) [Ti(C₂H₄O)₂N(C₂H₄OH), TBT] as a TiO₂ source. This paper reports preliminary results on the porous powders prepared from a starting solution with a Ti-to-Si atomic ratio of 1.0.

The starting solution was prepared by dissolving the solid (2-hydroxyethyl)trimethylammonium silicate prepared from 5 cm³ of tetraethoxysilane and 5 cm³ of a 50% aqueous solution of (2-hydroxyethyl)trimethylammonium hydroxide (The synthesis procedure was described previously.¹¹) in 10 cm³ of methanol, followed by the addition of 10 cm³ of the 2-propanol solution of TBT. The starting solution was stirred for 10 min at room temperature for intimate mixing and then held at 40 °C, which underwent gelation after ca. 12 h.

When (2-hydroxyethyl)trimethylammonium silicate alone

was dissolved in methanol, the solution did not undergo gelation in such a short time.¹² On the other hand, the gelation time of the methanol solution of (2-hydroxyethyl)trimethylammonium silicate and TBT was shortened by the addition of H₂O. These would indicate that the formation of hydrolysis product of TBT accelerated gelation of the solution.

The solution held at 40 °C was allowed for trimethylsilylation by the method of Lentz^{13,14} in order to investigate the distribution of silicate species present therein. The gas chromatogram of the product formed by the trimethylsilylation gives rise to one peak which is due to Si₈O₂₀[Si(CH₃)₃]₈. No peaks due to trimethylsilyl derivatives of low-molecular silicate species such as the monomer and dimer are found in the chromatogram, indicating that the Si₈O₂₀⁸⁻ species does not decompose in the solution. The yield of the Si₈O₂₀⁸⁻ silicate species is 15.7% for the solution at 5 min of holding at 40 °C, meaning that the rest of the SiO₂ component in the solution is present as higher-molecular-weight species than Si₈O₂₀⁸⁻. Briefly, the starting solution undergoes gelation without breakdown of the Si₈O₂₀⁸⁻ structure.

The gels thus obtained were dried at 50 °C for over 14 d to make their weight constant, and then heated in air at 650-1000 °C. The products were white powders.

The adsorption-desorption isotherms of the powders measured at -196 °C using N₂ indicate the type IV isotherm, suggesting the presence of mesopores. The porous properties of the products are shown in Table 1. Pore size distributions of

Table 1. The BET surface area, mean pore diameter, and pore volume of the SiO₂-TiO₂ porous substances obtained from the gels by heat-treatment in air at various temperatures for 1 h

| Heating Temperature / °C | BET Surface Area / m ² g ⁻¹ | Mean Pore Diameter / nm | Pore Volume / cm ³ g ⁻¹ |
|--------------------------|---|-------------------------|---|
| 650 | 496 | 4.1 | 0.50 |
| 800 | 373 | 4.2 | 0.40 |
| 900 | 282 | 4.1 | 0.30 |
| 1000 | 127 | 3.8 | 0.12 |

the powders, plotted with BJH method using desorption isotherm data, is rather broad. The diameter of main pores is in the range of 1-9 nm with a peak around the mean pore diameter shown in Table 1. The area and the pore volume decrease with increasing heating temperature of the precursor gels. Nevertheless, the surface area is 127 m² g⁻¹ even after calcination at 1000 °C, which is much higher than that of the SiO₂-TiO₂ porous glass-ceramics reported earlier.^{4,5}

Figure 1 (a)-(d) shows the XRD patterns of the powders formed by firing at 650-1000 °C in air for 1 h. Main peaks are ascribable to anatase and no obvious peaks are observed regarding rutile, implying that the TiO₂ component in the porous substances is dominantly present as anatase. The peaks

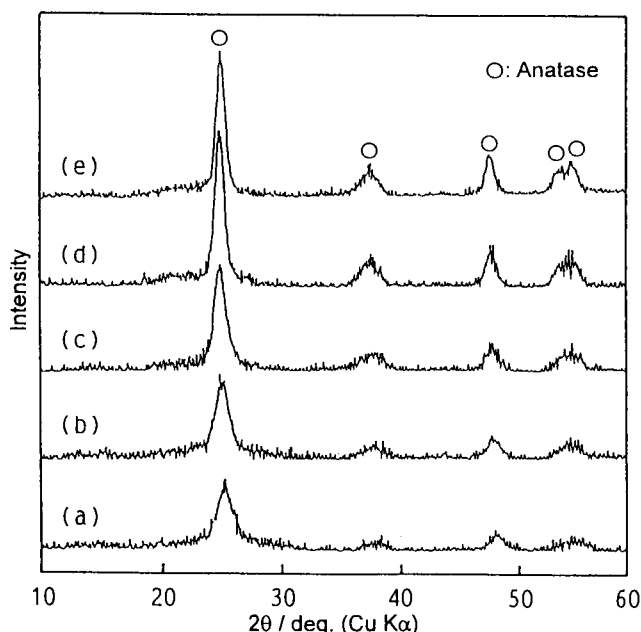


Figure 1. The XRD patterns of the $\text{SiO}_2\text{-TiO}_2$ porous powders formed by heating the gels in air at (a) 650, (b) 800, (c) 900, and (d) 1000 °C for 1 h and at (e) 1000 °C for 5 h.

becomes sharper with increasing heating temperature, meaning that the size of crystallites of anatase becomes larger with an increase in heating temperature. It should be noted, however, that anatase is the main crystalline phase in the product formed at 1000 °C as well. No peaks due to crystalline SiO_2 phases are seen in the patterns. Thus, a broad peak centered around 22° in the patterns would be assigned to the SiO_2 component of the substances, which is present in the amorphous state.

The solid-state ^{29}Si CP/MAS NMR spectra of the powders give rise to a main signal at -99.9 ppm which is due to the $\text{Si}(\text{OSi})_3(\text{O}^-)$ (Q^3) unit together with shoulders at -90.4 and -108.9 ppm. These shoulders would be assigned to the $\text{Si}(\text{OSi})_2(\text{O}^-)_2$ or cyclic Q^3 unit and $\text{Si}(\text{OSi})_4$ unit, respectively. The appearance of the shoulder at -90.4 ppm would indicate that some structural changes took place in the siloxane network during the heat-treatment. The fact that the Q^3 signal is dominant in the spectra, however, suggests that the structure of SiO_2 component of the porous powders may result from the structure of the SiO_2 source since the $\text{Si}_8\text{O}_{20}^{8-}$ species consists of the Q^3 unit solely.

The XRD pattern of the powders formed by heat-treatment

at 1000 °C for 5 h [Figure 1 (e)] gives rise to sharp peaks due to anatase. No apparent peaks due to rutile are seen. The transition temperature from anatase to rutile is not constant due to the coexistence of cations¹⁵ or anions.¹⁶ And, it was shown that anatase was the main crystalline phase precipitating upon heating sol-gel processing-derived $\text{SiO}_2\text{-TiO}_2$ gels at 1000 °C.¹⁷ The $\text{SiO}_2\text{-TiO}_2$ substances produced in this study, however, reveal high surface areas in addition to the presence of anatase at high temperatures, which would be the first example of high surface area materials consisting of anatase as the main component.

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