Microporous Structure of Titanium Oxide Prepared by a Salt Catalytic Sol–Gel Process

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A microporous structure (d_{pore} < 1 nm) of titanium oxide was synthesized by a salt catalytic sol–gel process of dilute titanium tetra-*n*-butoxide ($Ti(n\text{-}C_4H_9O)_4$) and H_2O solution without any template molecule. The specific surface area of titanium oxide after the calcinations at 300–350 °C was 310 $m^2\ g^{-1}$. It decreased significantly by calcinations above 400 °C because the microporous structure collapsed with crystallization into anatase.

Microporous materials have been applied for various fields such as catalysis, molecular sieving and selective adsorption. In particular, microporous structures of metal oxides were popular for silica-based oxides. Titanium oxides are potential materials applied for catalytic, photocatalytic, or photo-voltaic materials. Anderson and his collaborators have prepared microporous structures of titanium oxide by the peptization of TiO_2 fine particles.[1,2] Microporous titanium oxide xerogel with an average pore diameter below 1.4 nm was obtained from drying precursor gel, prepared by the modified sol–gel process using $Ti(OC(CH_3)_2C_2H_5)_4$. The aggregation of ultrafine particles make micropores among the particles by reducing both hydrolysis and condensation rates in the sol–gel process using large branched alkoxy groups. Although the peptization method is effective for preparing microporous structure, the mesopore was partly formed. In addition, it takes more than two months for the preparation. Much simpler method is required for preparing microporous titanium oxide.

Davis et al.[3,4] studies the synthesis of microporous Ti–Si mixed oxides (d_{pore} = 1–1.5 nm) by the sol–gel process with controlling the rate of additional water to a mixture of titanium isopropoxide and tetraethylorthosilicate in 2-propanol. Kosuge et al.[5] decreased the pore sizes (d_{pore} = 0.84–0.90 nm) using octylamine. The presence of Si has been required for preparing the microporous structure since the polycondensation of Ti species would be slow. We have previously demonstrated that salt catalysts such as ammonium carbonate or ammonium acetate accelerate polycondensation of titanium alkoxide in the sol–gel process effectively.[6–8]

Furthermore, we have revealed that the microporous structure (d_{pore} < 1 nm) of silica was synthesized by the salt catalytic sol–gel process of the dilute $Si(OCH_3)_4$ and H_2O solutions. This technique has a potential for preparing microporous structure of various metal oxides. In this study, a microporous structure of titanium oxide is synthesized by a salt catalytic sol–gel process of dilute titanium tetra-*n*-butoxide ($Ti(n\text{-}C_4H_9O)_4$) and H_2O solutions.

Under a nitrogen atmosphere, 2 mL of a butanol solution containing 12.5 mmol of titanium tetra-*n*-butoxide, and 2 mL of a butanol solution containing 12.5 mmol of ammonium acetate and 12.5 mmol of H_2O, were prepared. A sol–gel reaction started when the two methanol solutions were mixed to a total of 25 mL ($Ti(n\text{-}C_4H_9O)_4$: 0.5 M, H_2O: 0.5 M, and CH_3COONH_4: 0.5 M). Precipitation was obtained by stirring this solution at 25 °C for 24 h and kept at 65 °C for a week. The precipitation was dried at 70 °C for 24 h, and calcined for 90 min.

Figure 1 shows N_2 adsorption isotherm of the titanium oxides. The isotherm of titanium oxide calcined at 250 and 350 °C is of type I. The BJH pore size distribution suggests absence of mesopores. The pore diameter of titanium oxide calcined at 350 °C is about 0.4 nm with narrow distribution determined by the MP method.

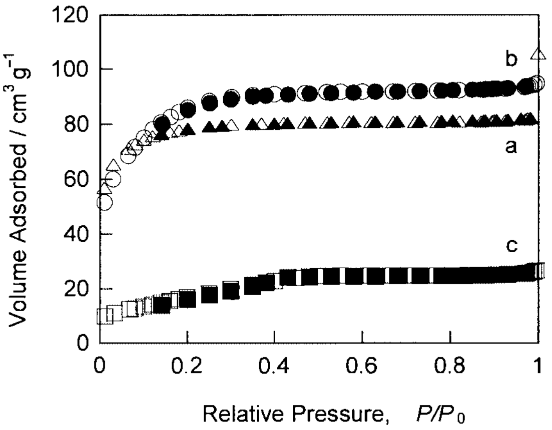

Figure 1. Nitrogen adsorption (open) –desorption (solid) isotherms of titanium oxides by the calcination at (a) 250 °C, (b)350 °C and (c)400 °C for 90 min.

Table 1 shows the specific surface area of titanium oxides calcined at various temperatures. The specific surface area of titanium oxide calcined at 300–350 °C was ca. 310 $m^2\ g^{-1}$. It decreased to 63 $m^2\ g^{-1}$ by the calcinations at 400 °C and to 4 $m^2\ g^{-1}$ at 450 °C.

Table 1. Specific surface areas of titanium oxides

Calcination temp. / °C	Specific surface areas / $m^2\ g^{-1}$
250	270
300	310
350	310
400	63
450	4
500	3

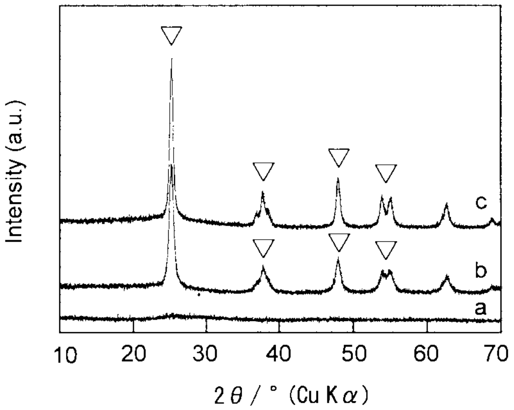

Figure 2. XRD patterns of titanium oxides by the calcination at (a)350°C, (b)400°C, (c)500°C. ▽: anatase

Figure 2 shows the XRD patterns of titanium oxide calcined at various temperatures. No peak was observed for titanium oxides calcined below 350 °C, while the peaks due to anatase appeared after the heat treatment at 400 °C. Therefore, amorphous titanium oxide crystallized to anatase at 400 °C.

Two steps of the mass loss were observed with exothermic peaks in the temperature range of 250–400 °C for the TG–DTA measurement of 20 K min^{-1}. They were due to pyrolysis of acetate and butoxy groups. Another exothermic peak was observed without any mass loss around 430 °C. It was due to the crystallization into anatase. Organic residues were partially deposited after the calcination at 350 °C for 90 min. The residues would prevent the particles from sintering which causes the decrease in the surface area and the formation of mesopores.

Titanium oxide was prepared by the salt-catalytic sol–gel process under dilute conditions of reactants, which has a larger number of micropores ($d_{\mathrm{pore}} < 1$ nm) but few mesopores. We need further investigation to clarify the properties of the microporous titanium oxide.

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