Low Temperature Synthesis of Titania Gel Containing Anatase and Rutile

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A crystallized titania gel was prepared without gel-collapse and precipitation by heat treatment at 348K for 24h of an aqueous ethanol solution of the Ti-peroxy compound obtained from $Ti(OiPr)_4$ and H_2O_2. The structure of the TiO_2 in the gel changed from rutile to anatase as the ethanol concentration in the gel increased.

Titanium dioxide (TiO_2) has various kinds of applications for environmental photocatalytic processes.[1,2] For example, the ability of anatase to photocatalytically decompose organic compounds is used to remove pollutants from air and water. In recent years, many methods for preparing fine anatase and rutile particles and thin films have been studied in order to develop photocatalysts with high catalytic activities.[3-5] It is important to develop simple and low temperature routes for preparing sols and gels containing anatase and rutile. Kominami et al. showed that mixtures of rutile and anatase precipitates can be obtained by the hydrothermal treatment of an alcohol solution of Ti alkoxides at 573K[6]. Ichinose et al. reported that a peroxo-modified anatase sol could be obtained by heat treatment of peroxo titanic acid solution above 373K[7]. If the crystallized titania wet gels were obtained, they could be the precursors of good nanoporous photocatalysts with high surface areas. In the present study, a low temperature method below 373 K for preparing a titania gel containing rutile and anatase fine particles is developed.

A titania gel containing rutile and anatase fine particles was prepared as follows: 30 wt% H_2O_2 solution was added to a 1 mol/L ethanol solution of $Ti(OiPr)_4$ (TTIP). The ratio, H_2O_2 : TTIP, was 12 : 1. A brown, clear solution was obtained. An aqueous ethanol solution (hereafter, referred to as the “diluting solution”) was added to this solution, which was heated at 348K for one of the following periods of time 3 h, 6 h, 12 h or 24 h. The solution became a gel after 1 h heating at 348 K. After heating for 24 h, collapse and precipitation of the gels had still not been observed. The shape of the obtained gel was cylinder (diamer 50 mm × height 50mm). This gel contains ca. 2 wt% crystallized TiO_2. The structure of the gel thus obtained was characterized by X-ray diffraction (Cu Kα 40 kV, 200 mA, Mac Science MXP-18). The peak broadening due to the apparatus was 0.06° ($2\theta = 30°$). FT-IR spectra of the gels after drying at 348K for 3 h were measured. The gel was peptized by adding an H_2O_2 solution and vigorously stirred at room temperature in order to analyze the particle size distribution in the gel. The particle size distribution was analyzed using a lazer-scattering particle size analyzer (HORIBA LA920).

The XRD patterns of the gels prepared using pure H_2O as the diluting solution are shown in Figures 1 (a), (b), and (c). Figure 1 (a) shows that the gel prepared by heating at 348 K for 6 h is anatase with poor crystallinity. The gels prepared by heating for 12 h and 24 h were mixtures of anatase and highly crystallized rutile as shown in Figures 1 (b) and (c). The XRD patterns of the gels prepared using pure ethanol as the diluting solution are shown in Figures 1 (d), (e), and (f). Figures 1 (d) and (e) show that the gel prepared by heating at 348 K for 6 h and 12 h contained anatase with poor crystallinity and that prepared by heating for 24 h was a more highly crystalline anatase. These results indicate that the formation of rutile and anatase occurred in the gels at 378 K without gel collapse and titania precipitation. The crystalline size in the gel obtained was calculated by using the Scherrer's equation and the FWHM of anatase (110) plane and rutile (101) plane. The crystalline size in the anatase gel increased from 4.8 nm to 10.1 nm and that in the rutile gel increased from 27.7nm to 40.8nm, when the heating time ranged from 12 h to 24 h. Figure 2 shows the relation between the anatase content in the titania gel and the molar fraction of ethanol in the diluting solution. The anatase content was estimated using the ratio, $I_A/(I_A+I_R)$, where I_A is the XRD peak intensity of the rutile (101) reflection and I_R is that of the anatase (110) reflection. It was shown that the amount of the rutile in the titania gel increased with increasing molar fraction of H_2O in the diluting solution.

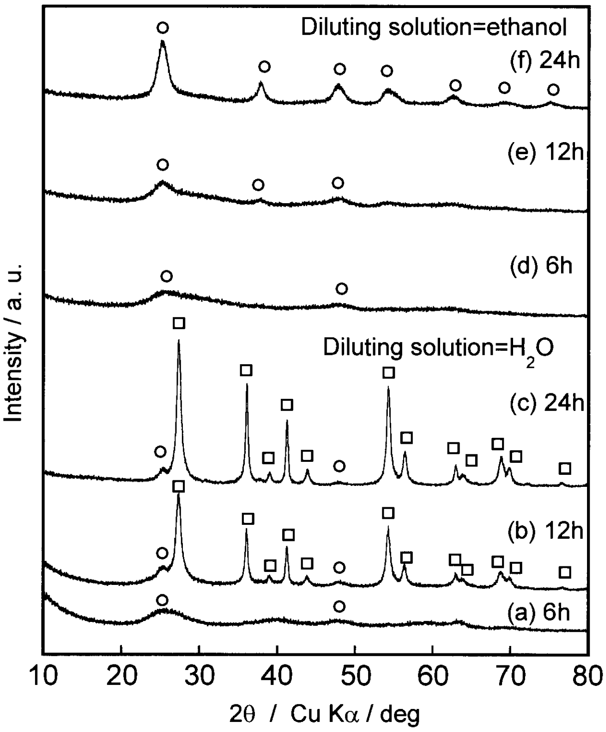

Figure 1. X-ray diffraction patterns of the titania gels. □ :rutile, and ○ :anatase.

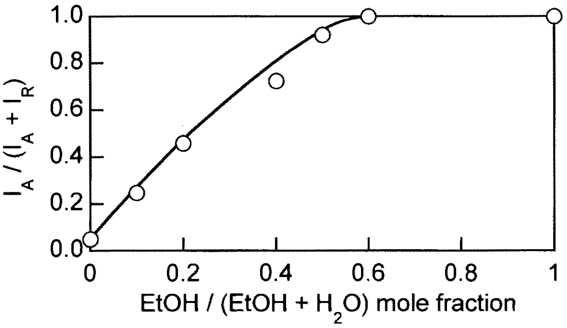

Figure 2. The relation between the anatase content in the obtained titania gel and the ethanol mole fraction on the diliuting solution.

In order to determine why the structure of the titania gels obtained depended on the diluting solution, the FT-IR spectra of the gels prepared by heating for 3h were measured as shown in Figure 3. The absorption from 3000 cm^{-1} to 3600 cm^{-1} in Figures 3 (a) and (b) can be assigned to the stretching vibration of the hydrogen-bonded OH groups. The absorptions around 1600 cm^{-1} and 1400cm^{-1} can be assigned to the antisymmetric and the symmetric stretching vibrations of COO^-, respectively. The COO^- was derived from the alcohol oxidized by the H_2O_2 in the gel. The absorption at 912 cm^{-1} and 717 cm^{-1} in Figure 3 (a) can be assigned to the stretching vibrations of the O-O bond and the Ti-O_2 bond of the peroxo group, respectively.[7,8] The absorption due to the peroxo group can not be observed in Figure 3 (b). We conclude that the peroxo group was consumed to oxidize the excess alcohol in the gel when the diluting solution was ethanol.

It is known that $Ti(OH)_4$ and H_2O_2 interact strongly and that a Ti-peroxy compound is formed.[9] When TTIP ethanol solution and H_2O_2 aqueous solution were mixed, $Ti(OH)_4$ was formed by the hydrolysis followed by the formation of the Ti-peroxy compound.[10] Tengvall et al. reported that the FT-Raman spectrum of a Ti-peroxy gel aged for 3 years showed the same spectrum as rutile powder.[9] Thus, they suggested the possibility of the formation of crystallized rutile at room temperature, however they cannot obtain well-crystallized rutile.[9] In this study, when H_2O was used as the diluting solution, Figure 3 (a) indicates that Ti-peroxy compounds were in the gel. Therefore, Ti-peroxy compounds play an important role in the formation of well-crystallized rutile in our gel as Tengvall et al. pointed out. The crystal structure of the titania gel obtained depends on the process of formation of OH or oxo bridges during olation or oxolation. The peroxo group in the hydrolyzed species of Ti ions and the amount of H_2O in the gel affects the olation and oxolation processes. Thereby, the crystallization process and the phase transition from anatase to rutile in the titania gel obtained depended upon the diluting solution.

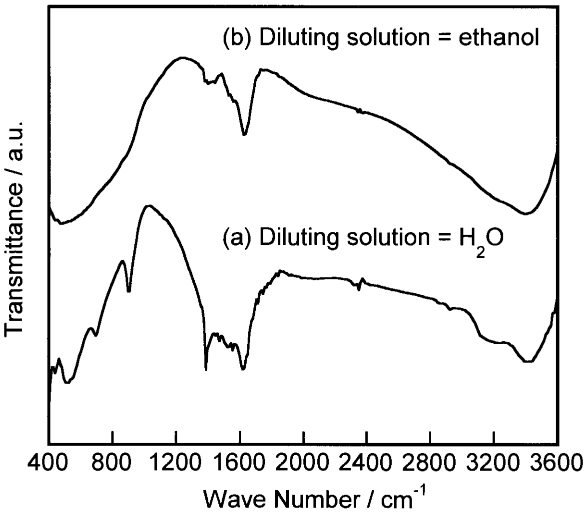

Figure 3. FT-IR spectra of the gels prepared by heating at 348K for 3h.

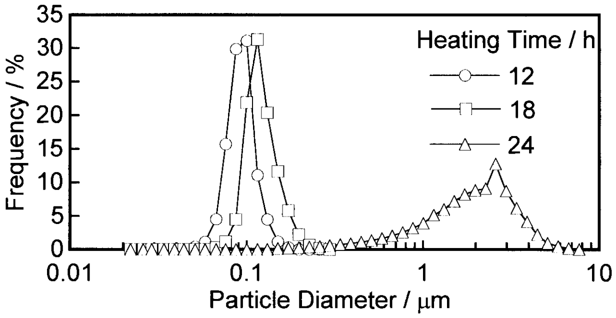

Figure 4. Particle size distribution of the titania particles in the peptized titania gel prepared by heating at 348 K. H_2O was used as the diluting solution.

Figure 4 shows the titania particle-size distribution in the sol obtained by peptizing the titania gel containing rutile prepared by using H_2O as the diluting solution. The average diameter of the rutile particles increased from 0.09 nm to 1.9 nm when the heating time was increased from 12 h to 24 h. On the other hand, the average diameters of the anatase particles were less than 0.02 nm that is the identification limit of the analyzer. Hence, the particle size and the crystal structure of the titania particles in the gel depended on both the diluting solution and the heating time.

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