CRYSTALLIZATION BEHAVIOR AND MICROMORPHOLOGY OF SOL-GEL DERIVED MESOPOROUS NANO-PARTICLES TITANIA

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ABSTRACT

CRYSTALLIZATION BEHAVIOR AND MICROMORPHOLOGY OF SOL-GEL DERIVED MESOPOROUS NANO-PARTICLES TITANIA. In this work, effects of drying methods on the micro-morphology ofmesoporpous TiO_2 prepared by the sol-gel method has been studied using transmission electron microscopy (TEM), X-ray diffraction analysis (XRD) and N_2 gas adsorption. Mesoporous TiO_2 consists of anatase nano-particles, about 5nm in diameter, have been obtained by hydrolysis of titanium alkoxide in a methanol solution and supercritical extraction in CO_2 at 60°C and 22Mpa. XRD peaks ofrutile have been found after annealing at 600°C. The particle sizes of anatase and rutile are about 13 and 25nm in diameter, respectively. The surface morphology of TiO_2 nano-particles has been discussed with the surface fractal dimensions estimated from the N_2 gas adsorption isotherms.

Key words : Sol-gel method, titania, crystallization, mesoporous material, fractal

ABSTRAK

KELAKUAN KRISTALISASI DAN MIKROMORPOLOGI NANO-PARTIKEL TITANIA MESOPORI DIPEROLEH DARI METODE SOL-GEL. Dalam penelitian ini, pengaruh dari metode pengeringan pada mikromorpologi dari TiO_2 mesopori yang dibuat dengan metode sol-gel telah dipelajari menggunakan, transmission electron microscopy (TEM), X-ray diffraction analysis (XRD) dan adsorpsi gas N_2. TiO_2 mesopori terdiri dan nano-partikel anatase, dengan diameter sekitar 5nm, telah diperoleh dengan menghidrolisa titanium alkoksida dalam larutan methanoi dan diekstraksi pada kondisi CO_2 superkritik pada tekanan 22 Mpa dan pada 60°C. Puncak - puncak XRD dan struktur mtil didapat setelah di bakar pada suhu 600°C. Ukuran diameter partikel dan struktur anatase dan rutil adalah berturut-turut sekitar 13 nm dan 25 nm. Morpologi permukaan dari TiO_2 nano-partikel telah dibahas dengan estimasi surface fraktal dimensions dari adsorpsi isothermal gas N_2.

Kata kunci : Metode sol-gel, titania, kristalisasi, material mesopori, fraktal

INTRODUCTION

Titania with high porosity and large surface area is attractive for various applications. The crystalline structure and surface morphology of porous ceramics are important for specific applications such as catalysts. Anatase type titania exhibits high photocatalytic activity and thus has recently attracted a great deal of attention in the field of photocatalysts for decomposition of environmental pollutants such as halogenated organic compounds [1] and for antifouling and antibacterial application [2, 3]. Anatase nanocrystals show higher photocatalytic activities than the bulk crystals because the nanocrystals facilitate the diffusion of excited electrons and holes toward the surface before their recombination [4]. However, the disadvantage of anatase titania for photo catalysis material is relatively low surface area, the low porosity and high temperature anatase formation. The most common pure anatase titania phase has small specific surface area [5], and anatase formation more than 400 °C [6,7].

The syntheses of ultrafine titania powders has been investigated using various techniques, including hydrothermal treatment, oxidation of titanium powder, and vapor decomposition [8-10]. The sol-gel method is widely used in preparation of transition metal oxides with nanoscale microstructures, and provides excellent chemical homogeneity and the possibility of deriving unique metastable structures at low reaction temperature. The high porosity and the high specific surface area of material prepared by the sol-gel method make them very attractive from catalytic point of view. Titania powders

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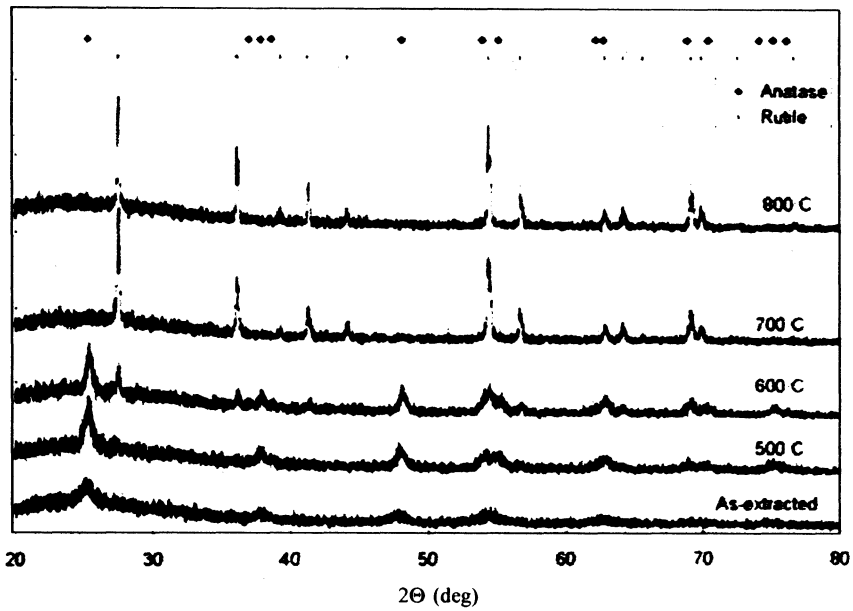

Figure 1. XRD patterns of the titania aerogel at various temperatures

prepared by the sol-gel method are usually amorphous, and they are crystallized by post-deposition processes, e.g. calcinations, hydrothermal treatment, etc. [11-13]. The supercritical extraction technique seem to be a good alternative to overcome the problems of high temperature anatase formation, low porosity and low surface area of anatase titania. Supercritical extraction techniques are recently used in material science to fabricate porous materials and hence their properties [14].

In this study, the effects of drying methods on the micromorphology and crystallization behaviors of sol-gel derived titania have been investigated. Mesoporous titania consists ofnanocrystalline anatase has been obtained by supercritical extraction at 60 °C and 22 Mpa using CO_2. In addition to TEM observations, surface fractal dimensions, DS, of titania nanoparticles have been estimated from the Nz adsorption isotherms by the method according to the Frenkel-Halsey-Hill (F-H-H) theory on multilayer adsorption [15].

EXPERIMENTAL

Titania wet gels were prepared by hydrolysis of $Ti(O\text{-}n\text{-}C_4H_9)_4$ (TNB) in a methanoi solution with acid catalyst. The molar ratio of TNB:H_20:methanol:HNO_3 used for the synthesis was 1:13.4:127:0.06. After aging at room temperature for 1 day, the wet gels were dried at 90 °C for 24h under an atmospheric pressure (the xerogel), dried after immersion in a surfactant solution (the modified gel), or supercritically extracted with CO_2 at 60 °C and 22 Mpa for 4h (in this paper called "the aerogel"). An ethanol solution of cetyltrimethylammonium chloride (CTAC, $C_{16}H_{33}N(CH_3)_3C1$, Kanto Chemical Inc., Tokyo), 1 mol/L, was used as the immersion solution of the modified gels [7]. After drying, the gels were annealed at temperatures up to 700 °C. The dried gels and the annealed gels were characterized by transmission electron microscopy (TEM, Philips, Teenai F20), measurements of Nz adsorption (Micromeritics, Tristar 3000), and X-ray diffraction (XRD, Rigaku, RAD-C). Using the N_2 adsorption isotherm, the surface fractal dimension, Ds, has been estimated by

$$\ln(V/Vo) = (-1/m)\ln[\ln(Po/P)] + \text{constant} \quad \ldots\ldots (1)$$

$$Ds = 3\text{-}1/m) \quad \ldots\ldots (2)$$

where V, V_0 and P/Po are the adsorbed volume of N_2, the saturation volume of adsorbed N_2 and the relative pressure, respectively [14].

RESULTS

X-ray powder diffraction of aerogel show anatase crystalline structure for as- extracted sample (Figure 1). The anatase structure was stable after calcination up to 500 °C for 2h. After calcination 600 °C for 2h, rutile structure with small intensity began to form. After calcination at 700 °C for 2 h, the anatase structure disappeared and pure rutile structure was formed completely. The XRD patterns of rutile did not change up to temperature calcination 800 °C.

The pore properties of the annealed gels are shown in Table 1. The average pore size, pore volume and specific surface area of the CTAC-modified gel are

Table 1. Pore properties of the gels annealed at 500 °C

Sample	BET surface area (m^2g^{-1})	Pore volume (m^3g^{-1})	Average pore diameter (nm)
Xerogel	39.9	0.0704	4.38
CTAC-modified Gel [15]	83.8	0.164	9.0
Aerogel	88.4	0.474	16.5

about twice larger than those of the xerogel. The pore volume and pore diameter of the aerogel are 7 times and 4 times larger than those of the xerogel, respectively.

Figures 2-5 show the TEM images of the aerogels. The as-extracted aerogels consist of nano-particles, about 5nm in diameter, and the lattice image of anatase is observed. Figure 3 shows the TEM images of the aerogels after annealing at 500 °C for 2h. The particle size increased to ca.13nm in diameter, and the lattice image of anatase is observed, too. Figure 4 shows the TEM images of the aerogels after annealing at 600 °C for 2h. Two kinds ofnano particles with different sizes were found.

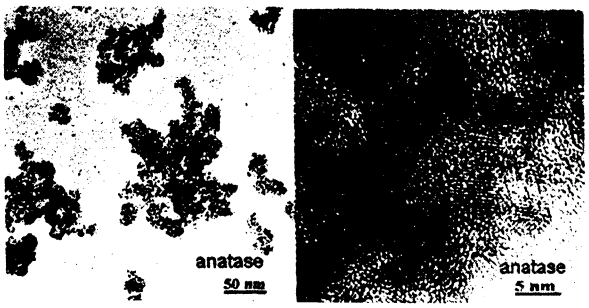

Figure 2. TEM images of the as-extracted aerogel

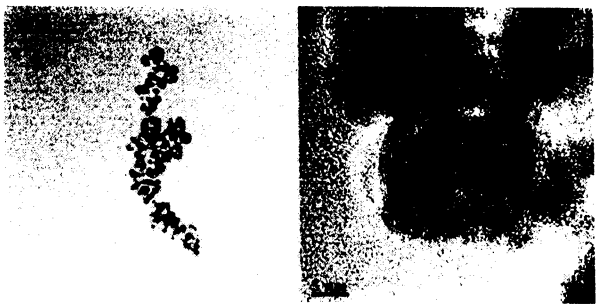

Figure 3. TEM images of the aerogel annealed at 500 °C for 2h

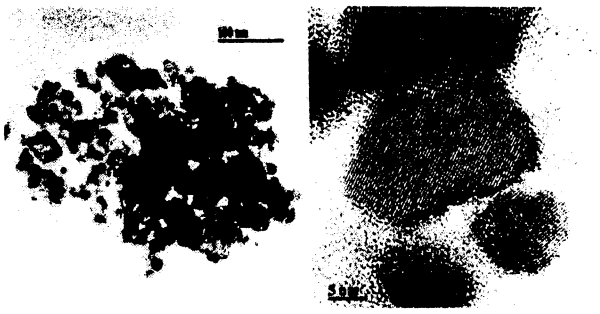

Figure 4. TEM images of the aerogel annealed at 600 °C for 2h

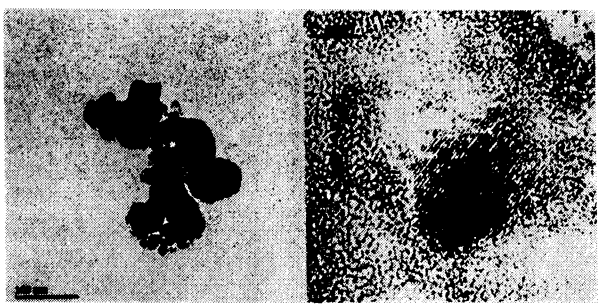

Figure 5. TEM images of the aerogel annealed at 700 °C for 2h

The lattice images show two crystalline phases, the larger rutile particles and the smaller anatase particles, about 25 nm and 13 nm in diameter, respectively (Figure 4). The results of XRD measurements also indicate these phases (Figure 1). After annealing at 700 °C (Figure 5), rutile phase with particle size about 90 nm in hexagonal form can beobserved.

The N_2 adsorption data are plotted according to Equation (1) in Figures 6 and 7 (F-H-H plot), and the D_s, values are estimated with Equation (2). The N_2 adsorption isotherm for the as-extracted aerogel indicates the mesoporous structure. The F-H-H plot shows two linear regions (Figure 6). The estimated surface fractal dimensions are about 2.49 and 2.68, both indicate rather complex surface morphology. The TEM observation suggests that there are amorphous and crystalline particles. Two values of D_s may be attributed to these two kinds of particles.

The surface fractal dimensions of the annealed aerogels are slightly larger than 2.5 as an example is shown in Figure 7, and almost the same as those of the annealed xerogels and the modified gels. After annealing at 700 °C or higher temperatures for 2h, the specific surface area decreased to 20 m^2/g or smaller. For these samples, adsorption isotherms were not obtained and the fractal analysis was impossible.

DISCUSSION

The as-dried xerogel and modified gel are amorphous by XRD, and the diffraction peaks of anatase are found after annealing at 500 °C. The crystallization behavior of titania gels was hardly affected by immersion in surfactant solutions [16]. On the other hand, anatase nanoparticles were observed for the as-extracted aerogels. Under a high pressure in supercritical CO_2 fluid, crystallization proceeded at low temperatures. During the supercritical extraction process, high pressure H_2O and alcohols also existed, and it might be possible that they affected the crystallization of titania gels. In general, anatase is formed at temperatures >400 °C [11]. It was previously reported [13] that the anatase phase was found for the TiO_2 film exposed to water vapor at 180 °C. It was considered that water vapor could promote the crystallization of the TiO_2 gels. The results of TEM observation show that the as-extracted aerogels consist of crystalline and non-crystalline nanoparticles, less than 10 nm in diameter. Anatase particles deposited at low temperature are smaller than those deposited at high temperature, at 500 °C or higher. After annealing at 500 °C, grain growth of anatase crystals in the aerogel was less significant than in the other gels. These results show that anatase nonoparticles, less than 10 nm in diameter, can be prepared by supercritical extraction of

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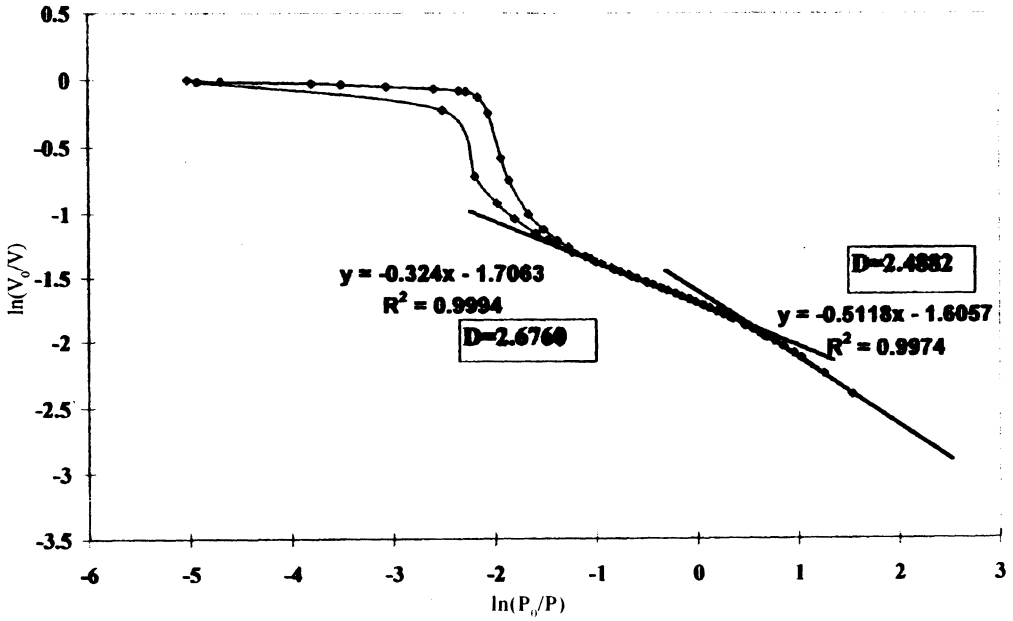

Figure 6. F-H-H plot of the as-extracted aerogel

titania gels using CO_2 fof longer time, and annealing at low temperatures.

The specific surface area, pore volume and pore size of the surfactant-modified gels and the aerogels are larger than those of the xerogels (Table 1). These values are smaller than the aerogels prepared by supercritical drying in ethanol, e.g. the specific surface area was about 100 m^2/g and pore radius was larger than 10 nm [17]. It may be expected that porous titania with better pore properties, larger surface area, porosity and pore size, can be obtained by the usual supercritical drying method, substitution of solvent with liquid CO_2 and supercritical drying. However, the supercritical extraction method of this study is a simple one-step-process and needs shorter processing time. The direct extraction of solvent in wet gels with supercritical CO_2 will be a good alternative method for the usual "aerogel" method.

The morphology of the TiO_2 aerogels was seen from Figures 2, 3, 4 and 5. Sample TiO_2 aerogel as-extracted, indicating the anatase structure (Figure 1) was found in small size and uniform (Figure2). The data of electron diffraction pattern, indicated clearly that anatase crystal phase with particle size is around 5 nm with d = 3, 62 Å was found. The morphology pure anatase seen from Figure 5, that the particles obtained at 500 °C is spherical and of uniform size, with grain sizes are around 13 nm for aerogel. After calcination at 600 °C, indicated interesting picture of aerogel, that is two

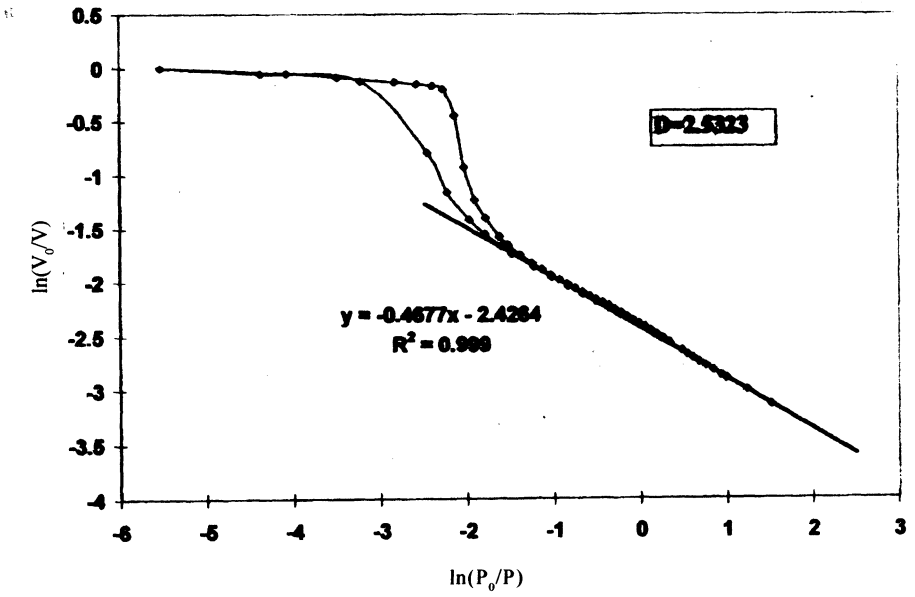

Figure 7. F-H-H plot of the aerogel annealed 600 °C

particles with difference sizes were found by TEM image and electron diffraction pattern (Figure 4). From that picture can be found two types of crystal with different phases and sizes namely anatase phase and rutile phase with particle sizes are around 13 nm and around 25 nm, respectively. Those phases also indicated by X-ray diffraction pattern for sample after calcination at 600 °C (Figure 1), that is show two type phase namely anatase phase and rutile phase. Crystal anatase phase that has small particle size and rutile phase has big particle size.

The pure anatase phase with particle size is around 13 nm in spherical form can be observed for sample after calcination at 500 °C in Figure 3, and pure rutile phase with particle size is around 90 nm in hexagonal form can be observed for aerogel sample after calcination at 700 °C in Figure 5. By TEM images and electron diffraction patterns can be observed crystal growth of anatase phase and phase transformation of anatase phase in spherical form to rutile phase in hexagonal form. The as-extracted aerogel sample is anatase phase in spherical form with particle size is around 5 nm, after calcination at 500 °C, that anatase will grow to bigger size of particle in the same form namely spherical form in size of particle is around 13 nm. After calcination at 600 °C, anatase phase did not grow that is in the same form and size namely spherical and around 13 nm, respectively, but phase transformation of anatase phase in around 13 nm size to be rutile phase in around 25 nm was occurred. After calcination at 700 °C, the complete of transformation from anatase phase to be rutile phase will occur, and rutile phase to grow to around 90 nm in size and hexagonal form.

The surface morphology of the gels was evaluated with the surface fractal dimension, D_s, estimated from the N_2 adsorption isotherms. In the range up to a few nm, D_s was about 2.5 for the crystalline samples annealed at 500 °C or higher temperatures. These values indicate that the crystalline mesoporous titania has rather complex shape of surface. After annealing at 600 °C, the crystalline particles grow larger, but the change in D_s is not significant. This result show the surface roughness of anatase particles hardly changed. After annealing at 700 °C or higher temperatures, titania transforms to rutile, and the specific surface area remarkably decreases. Then, the adsorption isotherms for the rutile samples cannot be obtained and the fractal analysis cannot be made. Two D_s values in two regions of the length scale for the as-extracted aerogel were found. The two regions are in near length scales, and the smaller D_s for the smaller region. This result suggests that there are two kinds of particles, probably amorphous and anatase particles as indicated by TEM observation (Figure 2). The smaller D_s was near to that of the sample annealed at 500 °C. It may be expected that crystalline particles have smoother surface with smaller surface fractal dimension. Thus the smaller particles may be crystalline, anatase. The low growth rate at low temperature, 60 °C, results in the formation of small crystalline particles.

CONCLUSIONS

The effects of the drying methods on the crystallization behaviors and micromorphology of sol-gel derived titania have been discussed.

1. Immersion in surfactant solutions before drying hardly affects the crystallization behavior and the surface morphology.
2. Supercritical extraction using CO_2 induced low temperature crystallization of titania gels. Nanoparticles of anatase, less than 10 nm in diameter, can be obtained at low temperatures.
3. The fractal analysis using N_2 adsorption isotherm makes it possible to evaluate surface morphology in nanometer scale.

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