PREPARATION OF POROUS TITANIA AEROGEL BY CO_2 SUPERCRITICAL EXTRACTION TECHNIQUE

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ABSTRACT

PREPARATION OF POROUS TITANIA AEROGEL BY CO_2 SUPERCRITICAL EXTRACTION TECHNIQUE . Porous anatase titania that is attractive to its notable functions for photo catalysis and photon-electron transfer. A method for producing the porous anatase titania at low temperature is with dissolving of a titanium alkoxide in a methanol to give a titanium alkoxide solution, adding a mixed solution containing water, nitric acid catalyst and a methanol to the titanium alkoxide solution to perform hydrolysis and simultaneous polymerization to give a polymer solution (gel). The solvent in wet gels was supercritically extracted in CO_2 at 60 °C and 22 Mpa. Thermal evolution of the microstructure of the gels were evaluated by TGA-DTA, N_2 adsorption, TEM and XRD. A porous titania, which has an anatase-form crystalline structure, an anatase-form particle diameter about 4 nm, average pore diameter of 13 nm, a BET specific surface area of 195 m²/g and a total pore volume of 0.55 cm³/g was obtained as prepared condition. The transformation of anatase phase to rutile phase occurred at 600 °C.

Key words : Supercritical extraction, sol-gel, aerogel, anatase titania.

ABSTRAK

PEMBUATAN AEROGEL TITANIA BERPORI DENGAN TEKNIK EKSTRAKSI SUPERKRITIK CO_2. Titania anatase berpori sangat menarik, berfungsi sebagai potokatalisis dan perpindahan poton-elektron. Metode untuk produksi anatase titania berpori pada suhu rendah, yaitu dengan melarutkan titanium alkoksida dalam metanol (larutan titanium alkoksida), hidrolisa dan polimerisasi yang simultan terjadi dengan menambahkan larutan campuran dari air, katalis asam nitrat dan metanol ke dalam larutan alkoksida untuk membentuk larutan polimer (gel). Pelarut dari gel basah di ekstrak pada kondisi superkritik dalam CO_2 pada 60 °C dan tekanan 22 Mpa. Evolusi termal dari mikrostruktur gel di evaluasi dengan TGA-DTA, adsorpsi N_2, TEM dan XRD. Titania berpori dengan struktur kriatal anatase dengan diameter partikel sekitar 4 nm, rata-rata diameter pori 13 nm, BET luas permukaan spesifik 195 m²/g dan volume pori-pori total 0,055 cm³/g telah didapat sebagai hasil ekstrak. Perpidahan fasa anatase ke fasa rutil terjadi pada 600 °C.

Kata kunci : Ekstraksi superkritik, sol-gel, aerogel, anatase titania

INTRODUCTION

One of the most important applications of the sol-gel method can be found in the field of catalysis. The most common sol-gel process involves the controlled hydrolysis of an alkoxide precursor followed by condensation to form a three-dimensional polymeric gel network. The high porosity and the high specific surface area of material prepared by sol-gel method, make them very attractive from catalytic point of view.

Titania has a chemical formula TiO_2 and is known to have a crystalline structure of anatase-form, rutile-form or amorphous structure. An anatase TiO_2 has been extensively investigated by scientists owing to its notable functions for photo catalysis and photon-electron transfer [1, 2]. On the other hand, rutile is a thermodynamically stable phase possessing smaller band gap energy (3.0 eV) than the anatase

phase (3.2 eV) [3, 4]. In photo catalysis research, chemists have been paying much greater attention to anatase TiO_2 than to rutile TiO_2 because anatase had been considered to be more active than rutile. A anatase titania which can be used as a catalyst for removal of nitrogen oxides, oxidation of organic substances, decomposition of dioxine compounds, or decomposition and removal of organic solvents, surfactant etc [5].

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 have small specific surface area that is less than 55 m²/g [6], and anatase formation more than 400 °C [7, 8]. 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.

In this study we report the synthesis and morphological of porous sol-gel derived titania aerogel which were prepared by CO_2 supercritical extraction and characterized. The titania xerogel dried under an atmospheric pressure was also prepared for comparison. We show that the anatase titania aerogel can be found at as prepared condition.

EXPERIMENTAL

Aerogel of anatase TiO_2 were prepared by hydrolysis of titanium n-butoxide $Ti(OC_4H_9)_4$ (TNB)in an methanol solution with acid catalyst. The molar ratios used for the synthesis were H_2O/alkoxide = 2, HNO_3/alkoxide = 0.06 and methanol/alkoxide = 12. The TNB was first dissolved in methanol and small H_2O at room temperature, and stirred for 30 min. After that, a mixture of the catalyst solution of methanol, H_2O and HNO_3 was added under continuous stirring. The solution gelled 2 minutes after the addition of the catalyst solution. The wet gel was aged at room temperature for 1 day and extracted by flowing supercritical carbon dioxide in a supercritical extraction system at 60 °C and 22Mpa. Changes in the microstructure of the gels during heating were evaluated using thermal gravimetric and differential thermal analyses (TG-DTA) and N_2 adsorption. TG-DTA measurements were carried out in a Seiko (Exstar 6000) TG/DTA 6200 System under airflow of 300 mLmin⁻¹, with heating rate of 10 °C.min⁻¹. The specific surface area, pore size distribution, and pore volume of gels, before and after annealing, were estimated by the Barret-Joyner-Halenda (BJH) method using N2 adsorption-desorption curves (Quantachrome, Autosorb). The pore and grain sizes of the samples were estimated from the image observed by Transmittance Electron Microscopy (TEM) (Philips, Tecnai F20). Crystallization behaviors of the samples observed by X-ray diffractometer (Rigaku, RAD-C) before and after calcination at 500, 600, 700, and 800°C respectively, were investigated.

RESULTS

For the aerogel, weight loss around 5 % was mainly observed at around 80 °C (Figure 1). Beyond 400 °C the sample of aerogel practically lose no more weight. In the DTA curve, the aerogel showed endothermic peak around 80 °C and weak triplet exothermic peaks around 150 °C and 250 which accompanied weight loss around 8% and 13% respectively. The broad exothermic peak at around 310 °C is followed by weight loss around 17% also observed. For the dried xerogel (Figure 2), weight loss around 10 %, 25% 30% and 37% were mainly observed at around 80, 250 350 and 450°C, respectively.
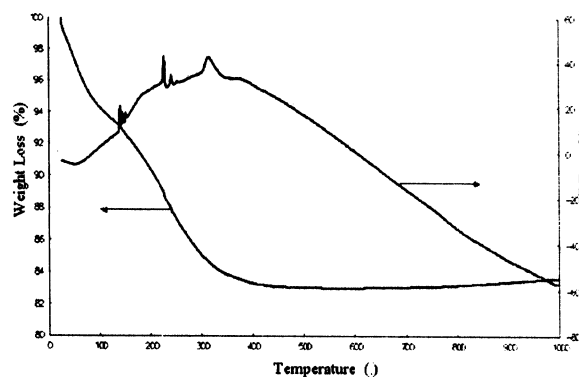
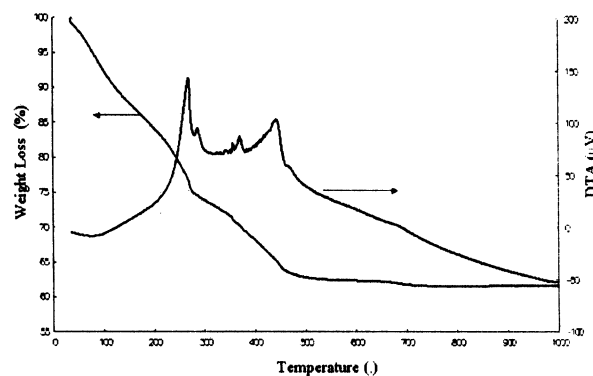*Figure 1.* TG-DTA pattern for the titania aerogel

Figure 2. TG-DTA pattern for the titania xerogel

Beyond 500 °C the sample of xerogel practically lose no more weight. In the DTA curve, the xerogel showed endothermic peak around 80 °C, and exothermic peaks around 250, 350 and 450 °C, respectively. Endothermic peaks appeared in almost the same temperature region namely at around 80 °C as the boiling point of water and methanol and ethanol as hydrolyzing reagent and solvent, respectively. Sharp exothermic peaks, which generally come from combustion of organic, appeared in higher temperature for xerogel namely at around 250 - 450°C than that of aerogel namely at around 150 - 310°C.
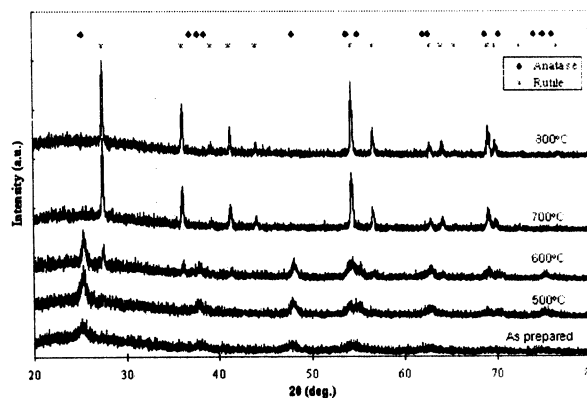
Figure 3. XRD patterns of the titania aerogel at various temperatures

X-ray powder diffraction of aerogel show anatase crystalline structure for as prepared sample (Figure 3). 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. X-ray powder diffraction of xerogel show amorphous phase after drying at 90°C for 24 h, as detected in their corresponding diffraction patterns (Figure 4). After calcination at 500 °C for 2 h, the amorphous phases of the sample change to anatase phase. After calcination 600 °C for 2h, the anatase structure almost disappeared and rutile structure with strong intensity was formed. Finally, after calcination at 650°C for 2 h, the pure rutile phase was observed.
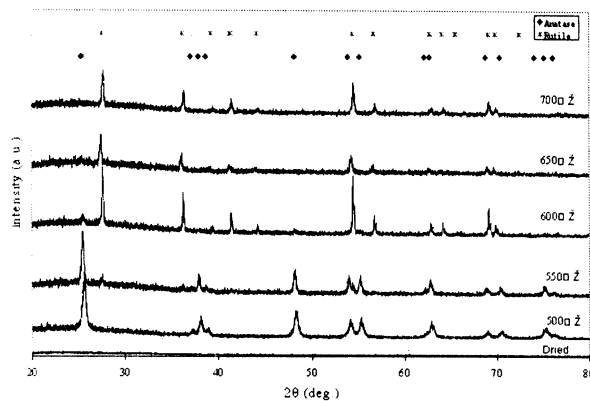

Figure 4. XRD patterns of the titania xerogel at various temperatures

Figure 5, Figure 6 and Figure 7 shows the TEM images and electron diffraction patterns of the structure TiO₂ aerogels as prepared, after calcination at 500°C, 600 °C and 700°C for 2h. Many small crystal of titania were observed throughout the as-prepared aerogels. The electron diffraction pattern also showed a weak orientation of titania crystals. The particle size of the TiO₂ aerogel as prepared was around 4 nm (Figure 5).
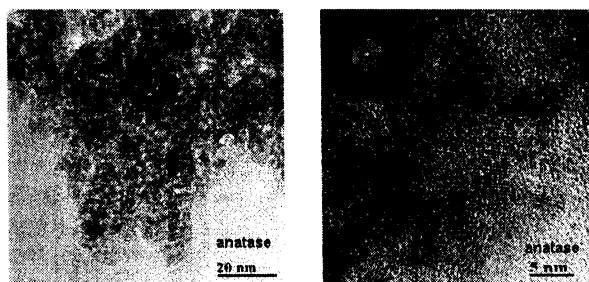

Figure 5. TEM image and electron diffraction pattern of aerogel as prepared

The particle size of the TiO₂ aerogel increases significantly, around 13 nm after calcination at 500 °C for 2h (Figure 6). After calcination at 600 °C, two crystalline shapes which their different particle size that

is around 13 nm and another is around 25 nm, were appeared clearly (Figure 6). After calcination at 700°C, the particle size increase drastically up to 90 nm and clearly appeared in the hexagonal form.
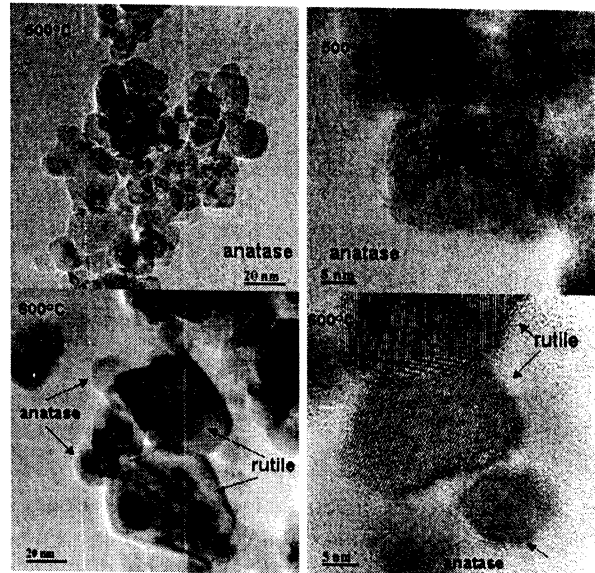

Figure 6. TEM images and electron diffraction patterns of aerogel after calcination at 500°C and 600°C
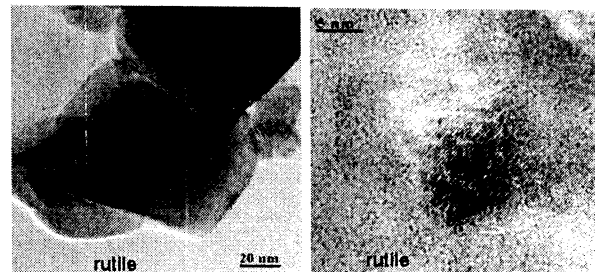

Figure 7. TEM image and electron diffraction pattern of aerogel after calcination at 700°C

Figure 8 shows the effect of calcination temperature on specific surface area of TiO₂ aerogel. After calcination at 500°C and more, the value of specific surface area of TiO₂ decrease drastically.
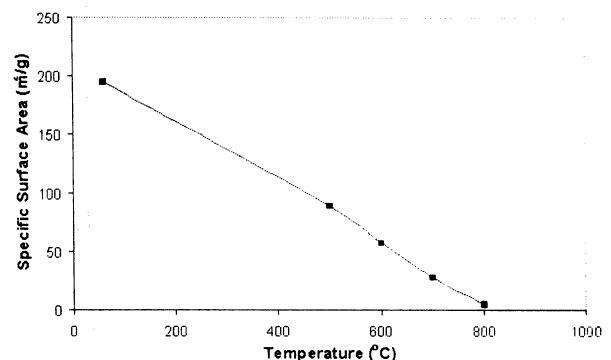

Figure 8. Effect temperatures calcination on specific surface area of titania aerogel

Figure 9 shows the effect of calcination temperature on pore volume of TiO₂ aerogel. After

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calcination more than 500 °C, the value of cumulative pore volume of TiO_2 did not change significantly. After calcination at 600 °C the pore volume decrease, and after calcination at 700 °C or more the pore volume of sample decrease even drastically.
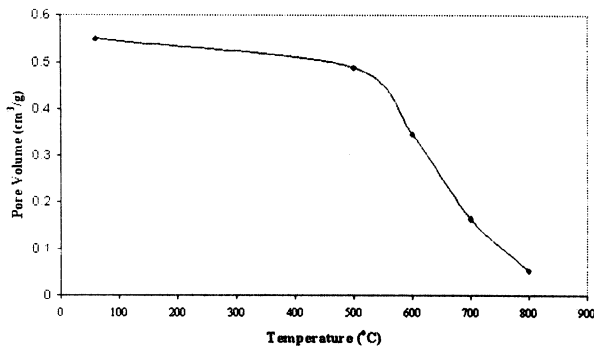

Figure 9. Effect temperatures calcination on pore volume of titania aerogel

Figure 10 shows the effect of calcination temperature on average pore diameter of TiO_2 aerogel. The average pore diameter of TiO_2 increase with increasing of calcined temperature. Average diameter increase gradually after calcination up to 600 °C, and increase drastically after calcination at 700°C and more.
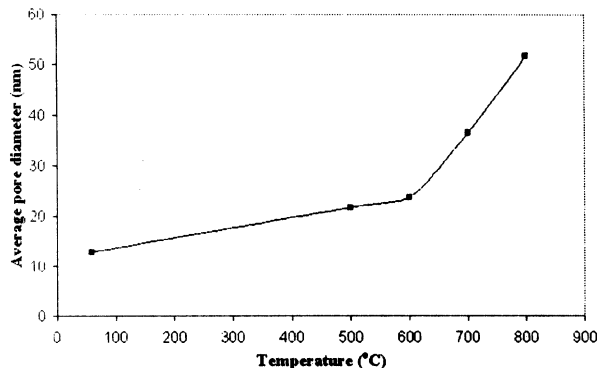

Figure 10. Effect temperatures calcination on pore diameter of titania aerogel
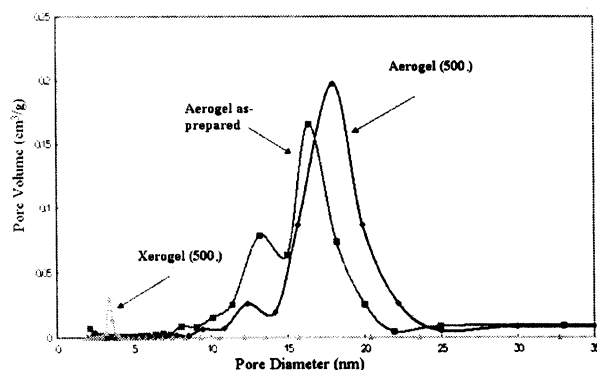

Figure 11. Pore size distribution of aerogels and xerogel as prepare and after calcination at 500°C

Figure 11 shows the pore size distribution of TiO_2 aerogel as prepared and after calcination at 500 °C, and

TiO_2 xerogel after calcination at 500 °C for 2h. The pore diameter of TiO_2 as prepared and after calcination at 500 °C were broader and around 4 time larger than TiO_2 xerogel after calcination at 500 °C. The pore volume distribution of the TiO_2 aerogel after calcination at 500 °C was bigger and broader than TiO_2 xerogel.

DISCUSSION

The temperatures to eliminate residual organic of the aerogel and xerogel are different (Figure 1 and Figure 2). The temperatures for combustion of residual organic for the aerogel up to 210 °C, is about 140 °C lower than that of the xerogel (Figure 1 and Figure 2). Exothermic peaks at temperatures higher than 310°C are hardly found for the aerogel. It may be caused by the residue organic that hardly remained in the TiO_2 aerogel. The most part of residue organics in the aerogel may be removed by the supercritical extraction. The temperature to eliminate residual organic of TiO_2 xerogel was observed up to 450 °C, that is indicated that a lot of residues organic still remain. This is caused by aerogel structure is more porous than xerogel structure. An organic residue which was trapped in xerogel pore was more difficult to be removed, because xerogel is more densified than aerogel. Beside that, it may be caused by different type of adsorbed residue organics into gels. The type adsorbed residue organics into gel of aerogel is physisorbed organic type and the type adsorbed residue organics into gel of xerogel is chemisorbed organic.

The effect of supercritical extraction toward crystallization can be seen on Figure 3. At high pressure extraction (22 Mpa), anatase crystal was formed, this will never happen if drying is being performed on ambient pressure (Figure 4). This result is interesting due to anatase structure is formed before calcination being executed. In the xerogel, structure of anatase is formed on the temperature of 500 °C (Figure 4). Moreover, by using supercritical extraction technique will bring a material with higher specific surface area and more porous than the material which is dried at ambient pressure. If anatase TiO_2 is calcined at the temperature of 600 °C, rutile structure will begin to grow and it should be noted that anatase transforms completely to rutile at 700 °C. The change from of anatase structure to rutile structure happens without any obstacles that are rutile structure has bigger crystal size than anatase structure (Figure 6). Anatase TiO_2 aerogel is more stable than anatase TiO_2 xerogel. This result is caused by the transformation of anatase structure into rutile structure which is prevented by the porous structure of anatase TiO_2 aerogel.

The morphology of the TiO_2 aerogels was seen from Figure 5, Figure 6 and Figure 7. Sample as-prepared, indicating the anatase structure was found in small size and uniform (Figure 3 and Figure 5). The data of

electron diffraction pattern, indicated clearly that anatase crystal phase with particle size is around 4 nm was found. The morphology pure anatase seen from Figure 6, that the particles obtained at 500 °C is spherical and of uniform size, with grain sizes are around 13nm. After calcination at 600 °C, indicated interesting picture that is two particles with difference sizes were found by TEM image and electron diffraction pattern (Figure 6). 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. That phases also indicated by X-ray diffraction pattern for sample after calcination at 600 °C (Figure 3), that is show two type phase namely anatase phase and rutile phase. Crystal anatase phase that small particle size and rutile phase with 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 6, and pure rutile phase with particle size is around 90 nm in hexagonal form can be observed for sample after calcination at 700 °C in Figure 7.

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-prepared sample is anatase phase in spherical form with particle size is around 4nm, 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 rutile phase in around 25 nm was occurred. After calcination at 700 °C, the complete of transformation from anatase phase to rutile phase will occur, and rutile phase to grow to around 90 nm in size and hexagonal form.

Figure 8 shows the effect of calcination temperature on specific surface area. The as-prepared sample has the biggest specific surface area namely 195 m^2/g. After calcination at 500 °C, the specific surface area will decrease drastically up to 90m^2/g. Due to the crystal growth of small anatase phase in around 4 nm size, to bigger anatase phase in around 13 nm that affected decreasing specific surface area of the sample. After calcination at 600 °C the specific surface area of sample will decrease to 87 m^2/g, this is due to the phase transformation from anatase phase to rutile phase which affected to change of particle size to 25 nm. Specific surface area will drop to19 m^2/g after calcining at 700 °C. This happened due to rutile crystal's growth with particle size is a round 90 nm.

Figure 9 and Figure 10 show the influence of calcination temperature on pore volume and pore diameter change. The change of pore volume is not significant up to calcination at 500 °C, namely from 0.55 Cm^3/g to 0.49 Cm^3/g, but after calcination at 600 °C, the pore volume will drastically decrease up to 0.35 Cm^3/g. This happened due to at 600 °C calcination temperature, the transformation of anatase phase to rutile phase was occurred, which the rutile particle size is big that will cause the pore volume decrease. After calcination up to 600 °C, the pore diameter increase gradually, from 13 nm to 24 nm (Figure 10). After calcination at 700 °C, the pore diameter increase drastically to 37 nm, and pore volume decrease drastically to 0.16 Cm^3/g. This is due to the transformation of anatase phase to rutile phase, which the change particle size occurs drastically.

CONCLUSION

1. The CO_2 supercritical extraction technique will provide for obtaining anatase crystalline with a smaller size and a more regular shape.
2. A porous titania, which has an anatase-form crystalline structure, an anatase-form crystallite diameter about 4 nm, average pore diameter of 13 nm, a BET specific surface area of 195 m^2/g and a total pore volume of 0.55 cm^3/g was obtained by CO_2 supercritically extracted at 333K and 22.4 Mpa.
3. The transformation of anatase phase to rutile phase occurred at 600 °C.

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