

THE STABILIZING OF ANATASE AEROGEL AT HIGH TEMPERATURE

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ABSTRACT

Stable anatase is attractive to its notable functions for photo catalysis and photon-electron transfer. Stable anatase TiO_2 containing amorphous SiO_2 aerogel was prepared by hydrolysis of $Ti(OC_3H_7)_4$ and $Si(OC_3H_7)_4$ in a 2-propanol solution with acid catalyst. The solvent in wet gels was supercritically extracted in CO_2 at 60 °C and 22 Mpa. Thermal evolutions of the microstructure of the gels were evaluated by TGA-DTA, N_2 adsorption and XRD. A stable anatase TiO_2 containing amorphous SiO_2 aerogel with a BET specific surface area of 365 m^2/g and a total pore volume of 0.20 cm^3/g was obtained as prepared condition. The anatase phase was stable after calcination up to 1000°C, and BET specific surface area, total pore volume and average pore diameter did not change significantly after calcination up to 900 °C.

Keywords: Supercritical extraction, sol-gel, aerogel, stable anatase structure.

INTRODUCTION

In recent years, research into the used of heterogeneous TiO_2 catalyst in photo electrochemical solar cells has shown considerable promise in generating a cheap route to harnessing solar radiation [1]. Generally, TiO_2 exists in three different crystalline phase: rutile, anatase and brookite. TiO_2 in the anatase phase appears to be the most photoactive and the most practical of the semiconductor for environmental application [2]. The anatase TiO_2 bulk materials have band gap 3.2 eV, that is large than that of the rutile TiO_2 [3, 4]. Photo catalytic activity strongly depends on the lifetime of the electron hole pairs generated by photo excitation. As the recombination probability is inversely proportional to the magnitude of the band gap, the lifetime is prolonged and results in a high photo catalytic activity in anatase phase [5].

However, the disadvantage of anatase phase for photo catalysis material is relatively low surface area and the poor stability of the structure at high temperature. The most common pure anatase titania phase have small specific surface area that is less than 55 m^2/g [6], and stable only below 500 °C [7]. Therefore, much attention has been paid to the applications of mixed oxides containing TiO_2 . SiO_2 is amorphous stable and has a high surface area. The mixed oxides of TiO_2 and SiO_2 seem to

be a good alternative to overcome the problems of the low surface area and unstable of the anatase structure catalysts. Furthermore, the photo catalytic activity of the anatase phase is influenced by many factors such as the preparation method, particle size, crystal microstructure, specific surface area, porosity etc. In order to obtain anatase phase material with highly photo catalytic activity, these factors must be carefully taken into consideration.

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 modern processes have been developed to refine and control the stability and phase formation of the anatase phase. 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. Moreover the supercritical extraction technique can be able to improve of the pore volume and specific surface area of anatase phase. Supercritical extraction technique using carbon dioxide are recently used in material science to fabricate porous materials and hence their properties [8].

In this work, a method to stabilize, anatase phase, pore size and specific surface area of anatase TiO_2 containing amorphous SiO_2 aerogel

was made by sol-gel synthesis and supercritical drying.

EXPERIMENTAL PROCEDURE

Stable anatase TiO_2 containing amorphous SiO_2 aerogel was prepared by hydrolysis of titanium tetra-n-butoxide $\text{Ti}(\text{OC}_4\text{H}_9)_4$ (TNB) and tetraethylortosilicate $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS) in a 2-propanol solution with acid catalyst. The molar ratios used for the synthesis were alkoxide: H_2O : solvent = 1:13.4:127 and HNO_3 /alkoxide = 0.06. The ratio of $[\text{TiO}_2]/[\text{SiO}_2]$ is 1/2 and 1/4 in mol. The TEOS was first dissolved in 2-propanol at room temperature, and a mixture of the catalyst solution, remaining 2-propanol, H_2O and HNO_3 was added, and then stirred for 30 minutes. After that, the TNB was added and then the catalyst solution was added under continuous stirring. The solution gelled around 3h after the addition of the catalyst solution. The wet gel extracted by flowing supercritical carbon dioxide in a supercritical extraction system at 60°C and 22 Mpa.

Changes in the microstructure of the aerogel 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 $10^\circ\text{C min}^{-1}$. The specific surface area and pore volume of aerogels, before and after calcining, were estimated by the BET and Barret-Joyner-Halenda (BJH) method [9] using N_2 adsorption-desorption curves (Quantachrome, Autosorb). Crystallization behaviors of the samples observed by X-ray diffractometer (Rigaku, RAD-C)

after calcination at 500, 600, 700, 800, 900 and 1000°C respectively.

RESULTS

TG and DTA profiles of aerogel TiO_2 and TiO_2 containing SiO_2 are showed in Fig. 1 and Fig. 2. For the TiO_2 aerogel, weight loss around 5 % was mainly observed at around 80°C (Fig. 1). Beyond 400°C the sample of TiO_2 aerogel practically lose no more weight. In the DTA curve, the TiO_2 aerogel showed endothermic peak around 80°C and weak triplet exothermic peaks around 150°C and 250°C 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 TiO_2 containing SiO_2 aerogel, weight loss around 6 % was mainly observed at around 100°C . Beyond 400°C the sample of TiO_2 containing SiO_2 aerogel lose practically no more weight. In the DTA curve, the TiO_2 containing SiO_2 aerogel showed 13% endothermic peak around 100°C and exothermic peak around 400°C accompanied weight loss around 18%. Endothermic peaks appeared in almost the same temperature region for both samples namely at around 100°C as the evaporation of water and 2-propanol as hydrolyzing reagent and solvent, respectively.

X-ray powder diffraction of TiO_2 aerogel show anatase crystalline structure for as prepared sample (Fig. 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 is beginning to form.

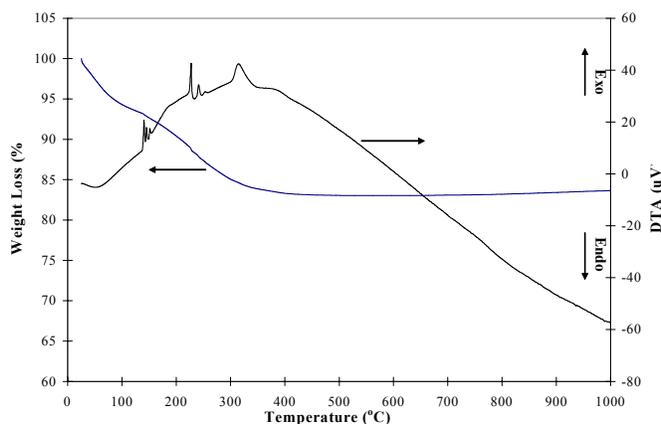


Fig 1 TG-DTA profile of TiO_2 aerogel

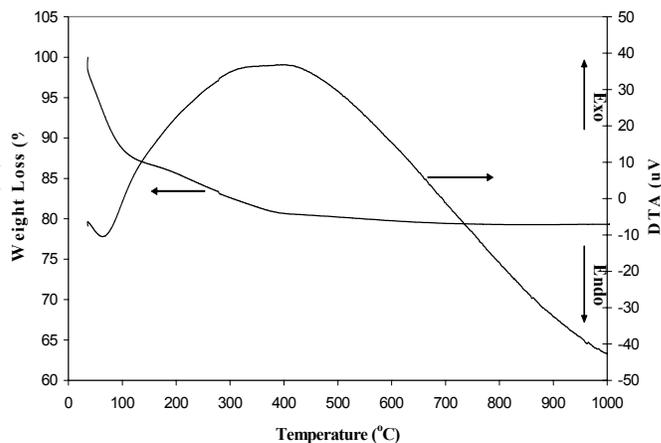


Fig 2 TG-DTA profile of $\text{TiO}_2/\text{SiO}_2$ aerogel

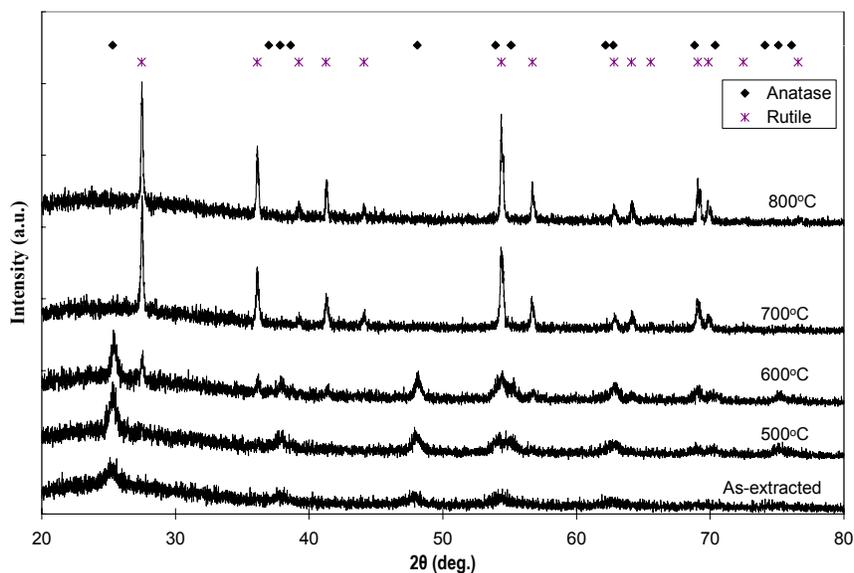


Fig 3 XRD patterns of the titania aerogel at various temperature

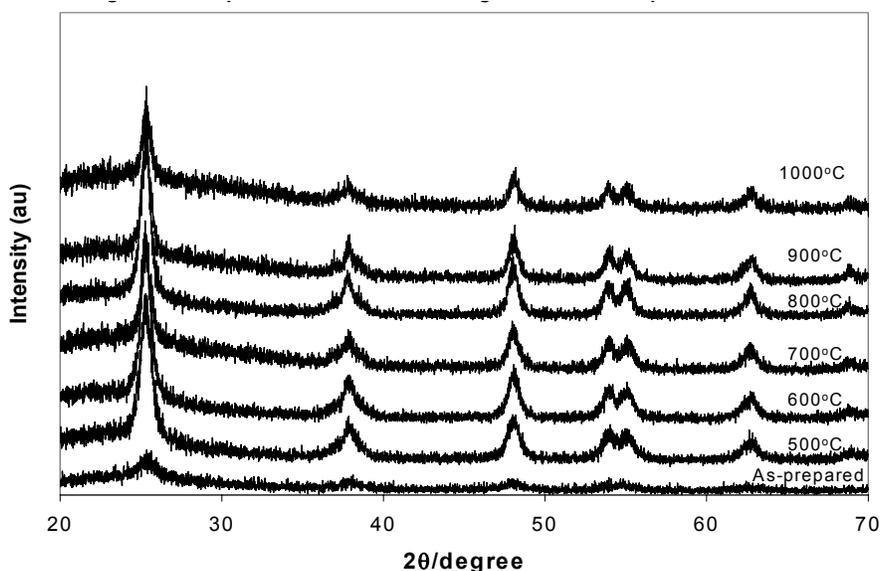


Fig 4 XRD patterns of the [TiO₂]/[SiO₂] = 1/2 aerogels as prepared and after calcination at various temperature

After calcination at 700 °C for 2 h, the anatase structure disappeared and pure rutile structure was formed. The XRD patterns of rutile did not change up to temperature calcination 800 °C. X-ray powder diffraction of TiO₂ containing amorphous SiO₂ aerogel with ration 1 : 2 in mol show anatase crystalline structure for as prepared sample as detected in their corresponding diffraction patterns (Fig.4). The anatase structure was stable after calcination up to 1000 °C for 2h. No rutile structure was observed. X-ray powder diffraction of TiO₂ containing amorphous SiO₂ aerogel with ration 1 : 4

in mol show amorphous structure for samples after calcination up to 900 °C, as detected in their corresponding diffraction patterns (Fig.5).

Fig. 6 shows the effect of calcination temperature on total pore volume of TiO₂ and TiO₂ containing amorphous SiO₂ aerogel. The total pore volume of TiO₂ as prepared is 0.56 cm³/g and after calcined up to 600 °C is 0.35 cm³/g larger than that total pore volume of TiO₂ containing amorphous SiO₂ aerogel, namely 0.25 and 0.28 cm³/g, respectively. After calcination more than 600 °C, the total pore volume of TiO₂ smaller than that of TiO₂

containing amorphous SiO₂. After calcination more than 500 °C, the value of total pore volume of TiO₂ decrease significantly, but did not change significantly for TiO₂ containing amorphous SiO₂

after calcination up to 800 °C for 2h. The total pore volume of TiO₂ containing amorphous SiO₂ was stable on high temperature, but not for TiO₂.

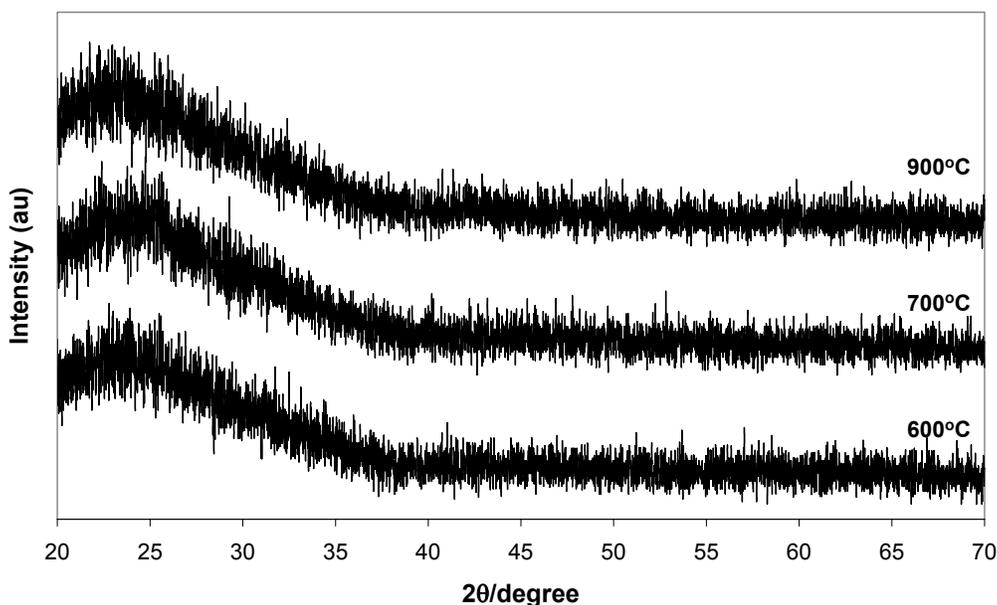


Fig 5 XRD patterns of the [TiO₂]/[SiO₂] = 1/4 aerogels after calcination at various temperature

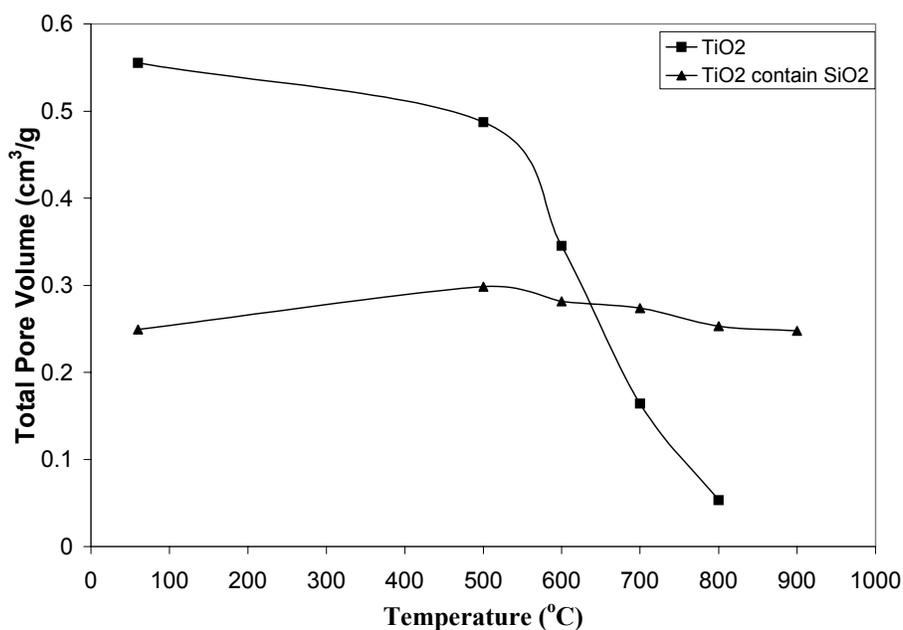


Fig 6 Cummulative pore volume of the TiO₂ and TiO₂/SiO₂ aerogels as prepared and after calcination at various temperature

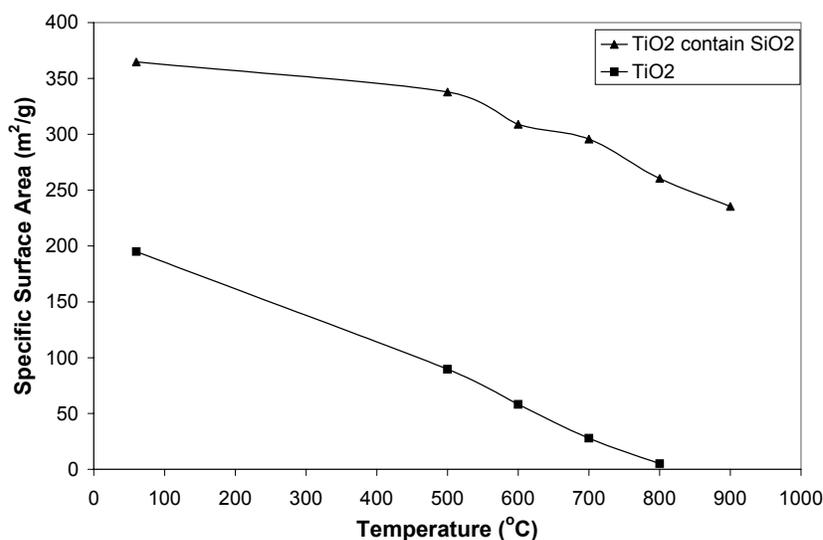


Fig 7 Specific surface area of the TiO₂ and TiO₂/SiO₂ aerogels as prepared and after calcination at various temperature

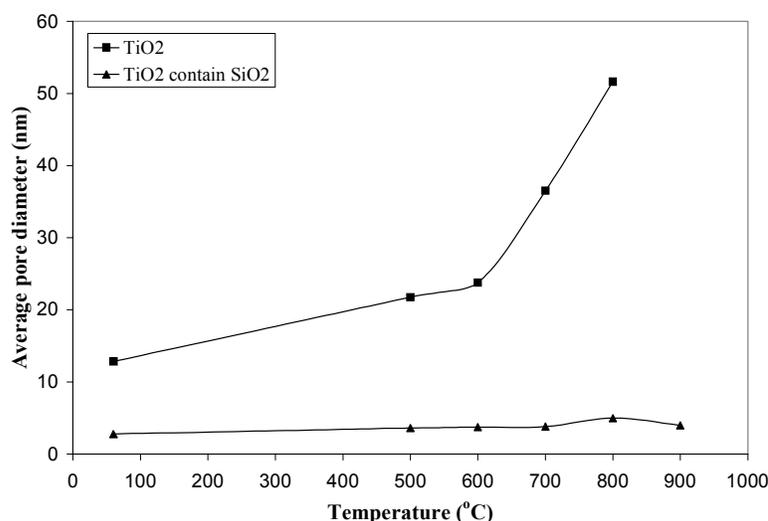


Fig 6 Average pore diameter of the TiO₂ and TiO₂/SiO₂ aerogels as prepared and after calcination at various temperature

Fig. 7 shows the effect of calcination temperature on specific surface area of TiO₂ and TiO₂ containing amorphous SiO₂ aerogel. The specific surface area of TiO₂ as-prepared is 195 m²/g and after calcined at 500 °C is 90 m²/g, smaller than that of specific surface area of TiO₂ containing amorphous SiO₂, namely 365 and 338 m²/g, respectively. The specific surface area of TiO₂ at all temperature calcinations is far smaller than that of specific surface area of TiO₂ containing amorphous SiO₂. After calcination at 500 °C and more, the value of specific surface area of TiO₂ decreases drastically, but does not change significantly for TiO₂ containing amorphous SiO₂. The specific surface area of TiO₂ containing

amorphous SiO₂ was stable on high temperature, but not for TiO₂.

Fig. 8 shows the effect of calcination temperature on average pore size diameter of TiO₂ aerogel and TiO₂ containing amorphous SiO₂ aerogel. The average pore size diameter of TiO₂ as-prepared is 12.8 nm and after calcined at 600 °C is 23.8 nm, larger than that average pore size diameter of TiO₂ containing amorphous SiO₂, namely 2.8 and 3.7 nm, respectively. After calcination at 700 °C for 2h, average pore size diameter of TiO₂ increased drastically namely 36.5 nm, but the average pore size diameter of TiO₂ containing amorphous SiO₂ did not change significantly, namely 3.8 nm. The average pore size diameter of TiO₂ as-prepared and after calcined up

to 800 °C is the larger than that of TiO₂ containing amorphous SiO₂. The average pore diameter of TiO₂ containing amorphous SiO₂ was stable at high temperature, but not for TiO₂.

DISCUSSION

The pattern of TG/DTA of TiO₂ and TiO₂ containing amorphous SiO₂ aerogels were almost same. There are peaks of DTA exothermic which were observed, but only one broad peak of DTA exothermic was observed for the TiO₂ containing amorphous SiO₂. The broad exothermic peak of the TiO₂ and TiO₂ containing amorphous SiO₂ aerogels around 400 °C (Fig. 1 and Fig.2) are almost same peaks high. Exothermic peaks at lower and higher temperatures than 400 °C are hardly found for the TiO₂ containing amorphous SiO₂ aerogel. It may be caused by the solvent (alcohol) that hardly remained in the TiO₂ containing amorphous SiO₂ aerogel. The solvent of the TiO₂ containing amorphous SiO₂ may be removed by the supercritical extraction. The exothermic peak at 400 °C is combustion of residual alkoxy group. The temperature needed to eliminate residual alkoxy group of TiO₂ aerogel were found up to 400 °C that is indicated that a lot of residual alkoxy group still remain.

The effect of CO₂ supercritical extraction toward crystallization can be seen on Fig. 3, 4 and 5. At high pressure CO₂ supercritical extraction (22 Mpa), crystal anatase was formed for both TiO₂ and TiO₂ containing amorphous SiO₂ aerogel with ratio 1 : 2 in mol aerogels, this will never happen if drying is being performed on ambient pressure. This result is interesting due to anatase structure is formed before calcination is being executed. In general the structure of anatase is formed on the temperature > 400 °C [10]. Previously reported that anatase phase can be found for TiO₂ film exposed to water vapor at 180 °C [11]. They reported that water vapor can be promoted the crystallization of TiO₂ gel. The same reason that CO₂ in supercritical condition can be promoted the crystallization of TiO₂ anatase. Moreover, by using CO₂ supercritical extraction technique will bring a material with higher specific surface area and more porous than the material which is dried at ambient pressure. On the other hand the sample of TiO₂ containing amorphous SiO₂ aerogel with ration 1 : 4 in mol is in amorphous phase, it is due to the high content of SiO₂ amorphous that will retard the crystallization and grain growth of TiO₂. The intensity of anatase TiO₂ and TiO₂ containing amorphous SiO₂ aerogels of as-prepared samples is almost same, but the intensity of anatase TiO₂ after calcination up to 600

°C, is weaker than anatase phase of TiO₂ containing amorphous SiO₂ aerogel, although the content of anatase TiO₂ is much larger. It is due to the solvent (alcohol) of the TiO₂ aerogel still exist (Fig. 1) so the crystal growth of anatase will be retarded.

If anatase TiO₂ 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. Anatase TiO₂ containing amorphous SiO₂ is more stable than anatase TiO₂. This result is caused by the transformation of anatase structure into rutile structure which is prevented by the existence of SiO₂ amorphous. Crystal of anatase TiO₂ is surrounded by SiO₂, because of that the growth of anatase to be rutile is blocked. No rutile appeared in the TiO₂ containing amorphous SiO₂ aerogel sample when the heat-treatment temperature was increased to 1000°C. Highly dispersed SiO₂ retards interface spreading of the phase transformation process and slow down the grain growth rate of the anatase, this effect prevented anatase from changing to rutile and still no rutile appeared in all samples, even at 1000 °C.

The specific surface areas of TiO₂ and TiO₂ containing amorphous SiO₂ aerogels under various calcination temperatures are illustrated in Fig. 7. It can be seen that with increasing calcination temperature, the specific surface areas decrease drastically for TiO₂ aerogel, but did not change significantly for TiO₂ containing amorphous SiO₂ aerogel. This is caused by the interaction of SiO₂ and TiO₂ ultra fine particles and growing of the particles is retarded.

CONCLUSIONS

The CO₂ supercritical extraction technique will provide for obtaining anatase crystalline. Highly dispersed SiO₂ amorphous can slow down the grain growth rate of TiO₂, and stabilize anatase, stabilize physical properties namely: specific surface area, pore volume and average pore size. No rutile phase appeared at calcination temperature up to 1000 °C.

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