JOURNAL OF MATERIALS SCIENCE **35** (2000) 6075–6079

Ambient-dried silica aerogel doped with TiO_2 powder for thermal insulation

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Two step-derived SiO_2 sol doped with TiO_2 powder dissolved in ethanol was prepared. After aging and washing of wet gel, surface modification with TMCS (trimethylchlorosilane) was followed to prevent additional condensation reaction during drying. Ambient-dried SiO_2-TiO_2 gel was heat-treated at various temperatures. The effects of the heat-treated temperature on the chemical bonding state of SiO_2-TiO_2 gel were investigated by means of FTIR and XRD analyses. After heat-treatment at 350 °C, crack-free SiO_2-TiO_2 gel was synthesized with density of 0.14 g/cm^3, porosity of 94%, and specific surface area of 613 m^2/g. Ambient-dried SiO_2-TiO_2 gel heat-treated at 350 °C exhibited thermal conductivities of 0.0136 W/m·K and 0.0284 W/m·K at room temperature and 400 °C, respectively. © *2000 Kluwer Academic Publishers*

1. Introduction

Due to unique properties such as low thermal conductivity (<0.02 W/m·K), dielectric constant (<1.7), refractive index (<1.1) and high surface area (>1000 m^2/g) resulting from their ultra-porous nature, silica aerogels can be applied in many directions [1]. Among proposed applications, silica aerogels have been intensively investigated and reviewed as potential candidates for possible application as a thermal insulating material. Since pure silica aerogels are translucent or transparent, the passive use of solar energy could be improved. Solar radiation passes through the aerogel layer and generates heat at the blackened surface of the wall. As the aerogel insulation is very effective, most of the heat is available for heating purposes.

It was presented that pure silica aerogels provide a total thermal conductivity of about 0.020 W/m·K under ambient conditions due to the extremely high porosity leading to a very low solid thermal conductivity [2]. Further, the nanometer-sized pores partially suppress the gaseous thermal transport. However, the radiative thermal conductivity of pure silica aerogels increases drastically with increasing temperature, as the specific absorption coefficient of SiO_2 is extremely low for wavelengths below 8 μm. Therefore reduction of the thermal conductivity of pure silica aerogel requires attenuation of radiative heat transfer for high-temperature applications. The thermal conductivity can be reduced if an opacifier such as titania powder, a strong broadband absorber, is added during the sol-gel process. The specific extinction of the opacified aerogel is drastically increase, especially in the range from 2 to 8 μm. Mineral powder integrated silica aerogels have total thermal conductivities of about 0.025 W/m·K at 300 K and 0.038 W/m·K at 800 K in air [2].

Supercritical extraction has been a conventional method to approach the synthesis of aerogel [3]. But since it not only costs much energy but also doesn't permit the continuous process, new synthetic methods of aerogel have been attempted to overcome the disadvantages of supercritical drying: ambient pressure drying [4–10]. Throughout silica sol-gel transition, condensation occurs continuously. The capillary force, resulting from the evaporation of pore fluids inside wet gel during drying, promotes shrinkage and induces irreversible additional condensation between neighboring -OH species. Consequently formed Si-O-Si bondings make shrinkage irreversible. Such an additional condensation at the wet gel state can be effectively retarded or prevented by developing non-reactive -CH_3 species by means of the surface modification with silane coupling agent such as TMCS (trimethylchlorosilane). Substitution of -CH_3 species for -OH also contributes to gel porosity to a degree. We presented the preparation of highly porous silica monolith and thin film by surface modification and modifying spin-coated wet gel [5–10].

In this work, we prepared aerogel-like silica gel monolith doped with 5 wt% TiO_2 powder at ambient pressure and examined the thermal conductivity suggesting the economic route to synthesis of opacified silica aerogel for high temperature thermal insulation.

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2. Experimental procedure

Silica sol was prepared by two-step acid/base catalyzed synthetic method. In the first step, TEOS (tetraethoxysilane, Fluka, Switzerland), ethanol (Ethyl alcohol, Duksan Co., Korea), H_2O and HCl were combined in the molar ratio $1:3.5:1:0.7 \times 10^{-3}$ and refluxed at room temperature for 90 min. In the second step, 5 wt% of anatase TiO_2 powder (TiO_2 KA-100, Korea Titanium Co., Korea; mean particle size $= 0.3\ \mu$m) dissolved in 30 ml of ethanol and 0.2 ml of 0.05 M NH_4OH were added into 50 ml of stock solution and mixed for 20 min. The concentration of the catalyst controls the gelation period in the sol-gel process and the nanostructure of the derived aerogels. In order to avoid sedimentation of the TiO_2 powders, the gelation period was limited to about 2 minutes after pouring the sol into the Teflon molds.

After four days of aging in TEOS/EtOH solution at room temperature to strengthen the gel network structure, the pore fluids in wet gel were exchanged with ethanol and *n*-hexane (Duksan Co., Korea) by turns to facilitate following surface modification. Subsequent modification was proceeded by immersing wet gel under 10 vol% TMCS (Trimethylchlorosilane, Lancaster Co., England)/*n*-hexane solution at 30 °C for 96 h. Modified wet gel was washed in *n*-hexane at 30 °C for 72 h, dried at 30 °C/72 h, 60 °C/48 h and heat-treated at various temperatures in the range of 200–1000 °C. Heat-treatment was executed as following; 1 K/min to 250 °C soaked for 2 h and 0.5 K/min to final temperature. These monoliths were denoted as 5STA.

Differential thermal analysis (DTA; TG/DTA-92, Setaram, France) was used to predict the reaction inside gel during heat treatment. Apparent density was determined by weighing samples of known dimensions. The microstructure of gel was observed by scanning electron microscopy (SEM; Hitachi, H4200, Japan) and transmission electron microscopy (TEM; 200 kV, JEOL, JEM-2000EX II, Japan) to present the distribution of TiO_2 powders between silica gel network. Nitrogen gas adsorption analysis (Micrometrics, Gemini 2375, U.S.A.) at 77 K was used to determine the specific surface area and pore size distribution of the gel. The specific surface area was determined using multipoint BET analysis and pore size distribution was determined by the BJH model [11]. Fourier transform infrared spectroscopy (FTIR; Jasco, FTIR-300E, Japan) was employed to investigate the change of chemical bonding state of gel according to heating temperature. Crystalline phases of the gels were identified using an X-ray diffractometer (Rigaku D/MAX Rint 2000, Japan; Cu-K_α, 30 kV, 16 mA). Thermal conductivity of the gel was measured using the transient hot wire technique [12], in which a platinum hot-wire was squeezed between a pair of cylindrical gels.

3. Results and discussion

The key problem of synthesizing 5STA is the preservation of well-dispersed sol state to prevent sedimentation of TiO_2 powder. This depends on the deflocculation and stability of filler which can be achieved by controlling the mixing time of the powders into the solution and the gelation time. In sol-gel process it is clear that gelation time is proportional to the amount of basic catalyst and inversely proportional to solvent amount. Therefore sol composition was optimized by the condition of EtOH/TEOS = 5 and NH_4OH/TEOS = 0.002 in molar ratio after preliminary experiments in which various amounts of solvent and catalyst were attempted, making agglomeration-free 5STA effectively. Fig. 1 shows TG/DTA curve of 60 °C-dried 5STA that experienced surface modification. Endothermic peak and weight loss around 140 °C is considered to be the evaporation of adsorbed water molecules. It is believed that the exothermic peak and weight loss in the vicinity of 250 °C are attributed to oxidation of -CH_3 developed from modification and residual organics (-OC_2H_5) [8]. The heating rate before and after 250 °C should be controlled to maintain monolithicity of 5STA as oxidation of organic species could exert stress on the gel network. In order to maintain monolithicity of 5STA, 2step heat treatment was executed as following; 1 K/min to 250 °C soaked for 2 h and 0.5 K/min to final temperature.

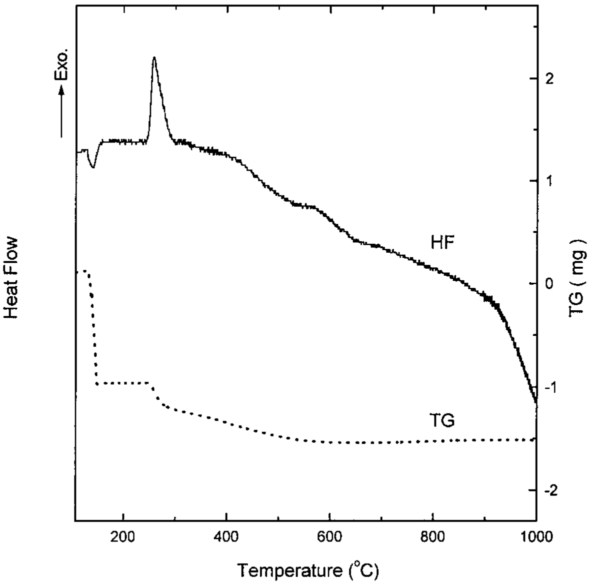

Figure 1 TG/DTA curve of 60 °C-dried 5STA in air (1 K/min).

Fig. 2 presents the influence of temperature on apparent density and porosity of 5STA. As temperature increases up to 350 °C, density gradually decreases. Whereas the gel, in which additional condensation occurs aggressively during drying, exhibits irreversible shrinkage, the gel with substituted -CH_3 species finally leads to spring back phenomenon during heat treatment, resulting in reversible shrinkage. Such a phenomenon has been already exhibited visibly through ambient-dried SiO_2 aerogel prepared under the same process as 5STA [5, 8, 10]. It is difficult for the gases in gel to escape due to the entangled structure of gel. Therefore it is thought that gel network is compressed by the gases which are expanded during heat treatment. It is expected that the continuous weight loss from near 250 °C (shown in Fig. 1) contributes to the decreasing tendency of density with heating temperature. Consequently surface-modified gel shows higher pore volume and accordingly lower density. After 350 °C density

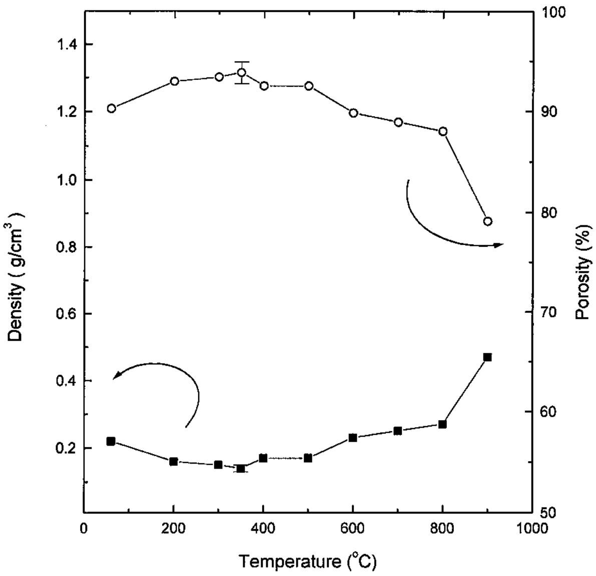

Figure 2 The evolutions of density and porosity of 5STA accoridng to various heating temperatures.

increases gradually and drastic increase is shown after 800 °C due to partial sintering of the gel.

Fig. 3 illuminates the microstructure of 5STA observed by means of SEM/TEM. 5STA exhibits 3-dimensional network structure which contains 60–70 nm spherical solid clusters and pores below 100 nm between them. Powders are somewhat in aggregated state. From the TEM plan view TiO_2 powders are physically embedded inside of 5 nm-sized silica gel. This is good agreement with the following FTIR result in which Si-O-Ti chemical bonding does not appear.

Pore size distributions of 5STA with various heating temperatures are shown in Fig. 4. Pore size lies in the range of 1–30 nm regardless to heating temperature. This is similar to pore size distribution of the conventional aerogels [4].

The texture of aerogels consists of an assembly of primary particles connected to form clusters. These clusters aggregate to establish the solid network. Schematically, pores belong to three family of sizes. Micropores are mainly located between primary particles. Mesopores are associated to pores located between the arms of clusters and the largest pores must be associated to volume located between clusters. The routes to perform densification act on different textural entities. Sintering induces a matter transport which results in an increase of primary particle size. As micropores disappear, mesopores size decreases. Accordingly, the largest-scaled pores also decrease in size. The net result of sintering is a rapid decrease in the specific surface area which must associated with micropore vanishing.

Fig. 5 displays the evolution of specific surface area of 5STA heat-treated at various temperatures. The specific surface area increases up to the maximum value of 613 m^2/g with increasing temperature in the range of 350–400 °C. This results from the spring back phenomenon via surface modification and the decrease of steric effect which hinders nitrogen adsorption due to oxidation of surface organic species [5, 8]. After this temperature specific surface area decreases gradually and drastic decrease is shown after 800 °C due to densification of the gel.

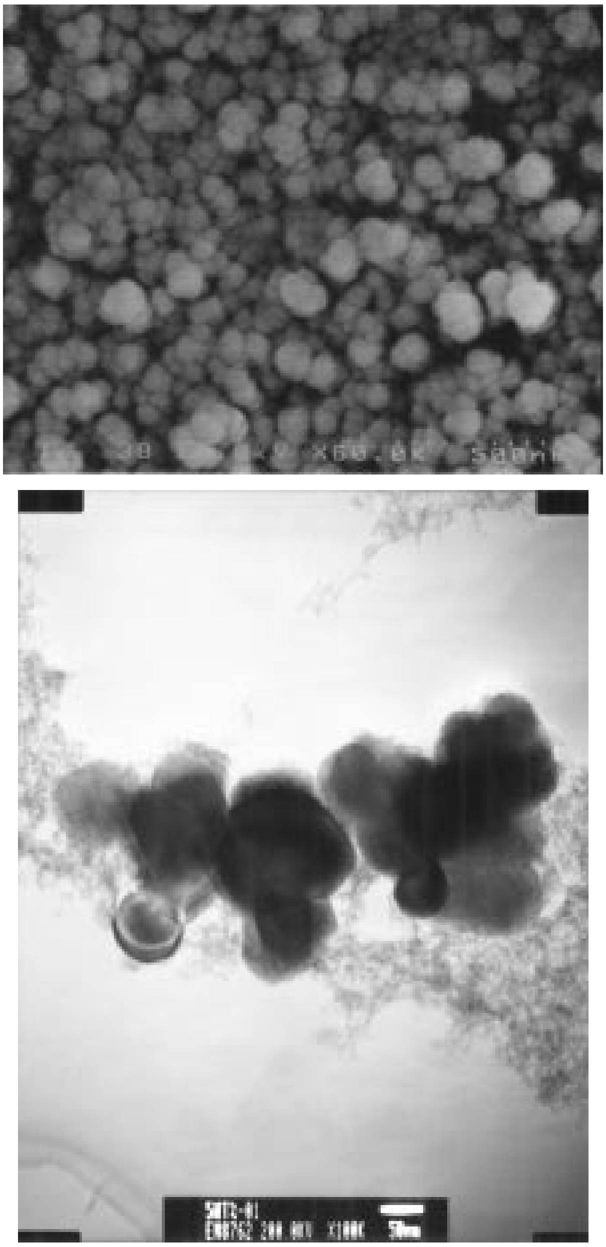

Figure 3 SEM/TEM images of 60 °C-dried 5STA.

FTIR spectra of 5STA heated at different temperatures are indicated in Fig. 6. Peaks near 1100 and 670 cm^{-1} are attributed to Si-O-Si and Ti-O-Ti bonding, respectively. While the 2923 and 1523 peaks indicate C-H bonding due to the presence of ethoxy groups ($-OC_2H_5$), the 2965 and 844 cm^{-1} peaks C-H bonding due to the presence of $Si-CH_3$ [13]. The remarkable change of peak lies in C-H bondings. Even though a considerable amount of $-CH_3$ species remains still in the case of 350 °C-heated 5STA, the oxidation of pyrolyzed $-CH_3$ to -OH species occurs dominantly in the 5STA heated above 500 °C. It is observed that $-CH_3$ species decrease with temperature but do not disappear completely with heat treatment up to 800 °C. As shown in DTA curve, the continuous exothermic reaction proceeds to ∼800 °C. It is clear from this result that the oxidation of organic groups ($-CH_3$, $-OC_2H_5$) is consecutively kept on even to ∼800 °C.

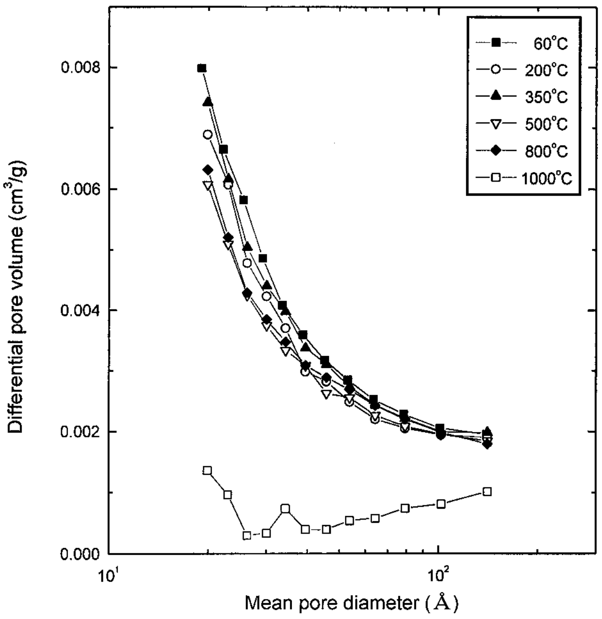

Figure 4 Pore size distributions of 5STA accoridng to various heat-treatment temperatures.

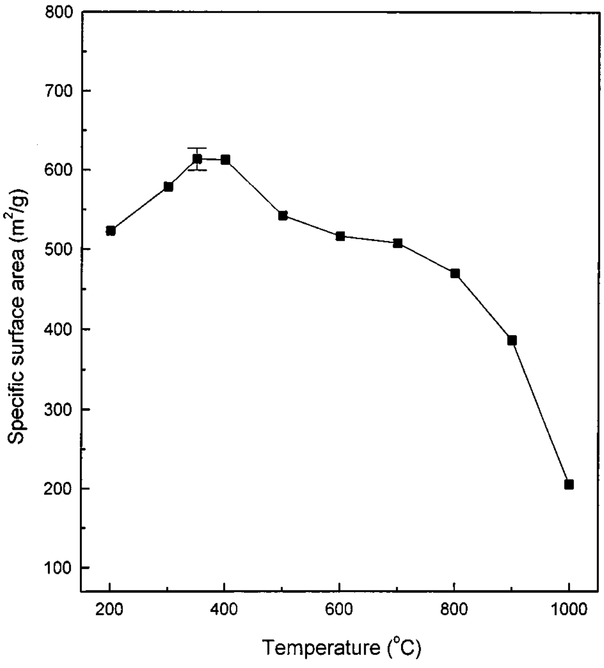

Figure 5 The evolutions of specific surface area of 5STA accoridng to various heat-treatment temperatures.

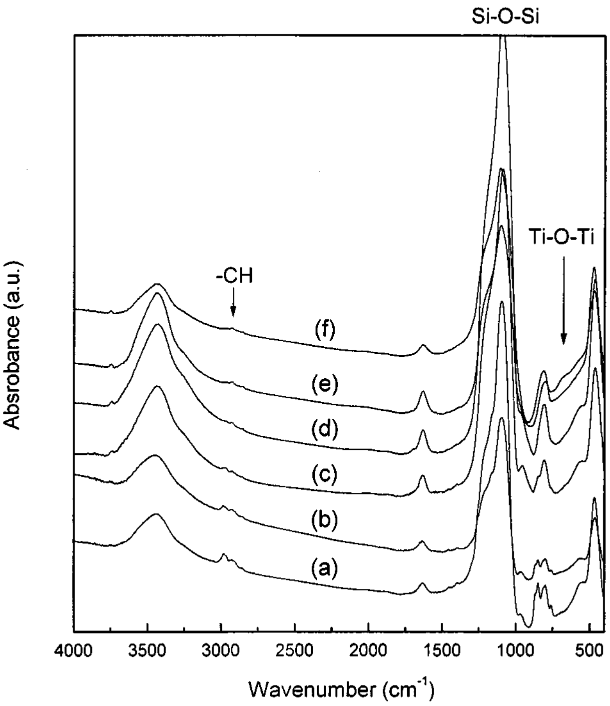

Figure 6 FT-IR spectra of 5STA accoridng to various heat-treatment temperatures; (a) 60°C, (b) 200°C, (c) 350°C, (d) 500°C, (e) 800°C and (f) 1000°C.

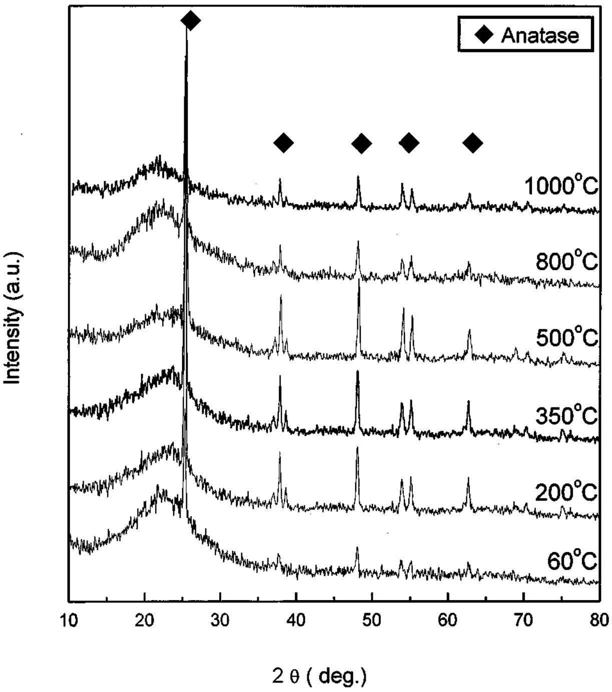

Figure 7 XRD patterns of 5STA accoridng to various heat-treatment temperatures.

XRD patterns of 5STA according to heating temperature (exhibited in Fig. 7) show halo in the range of 20–30° corresponded to amorphous silica gel and anatase characteristic peaks due to opacifying TiO_2 powders. There are no phase transitions between anatase and rutile with increasing heat-treatment temperature, agree with DTA result.

The total thermal conductivity in aerogel can be described by the sum of three contributions; the solid thermal conductivity, the gaseous thermal conductivity and the radiative thermal conductivity. The solid conductivity of aerogel is a factor of several hundred smaller than the conductivity of dense vitreous silica. This is expected because of the large amount of missing mass which restricts the propagation of local excitations to the chains in the tenuous structure. One way lowering the thermal conductivity of an aerogel is to suppress the gaseous conduction [1]. In this work evacuating 5STA down to 1 mbar of air pressure reduces the thermal conductivity to 0.0067 (heated at 350 °C) and 0.0138 W/m·K (heated at 800 °C) at room temperature, respectively. This value is believed as only solid conduction of 5STA [14].

Fig. 8 shows total thermal conductivity of pure silica aerogel and 5STA in air as a function of temperature.

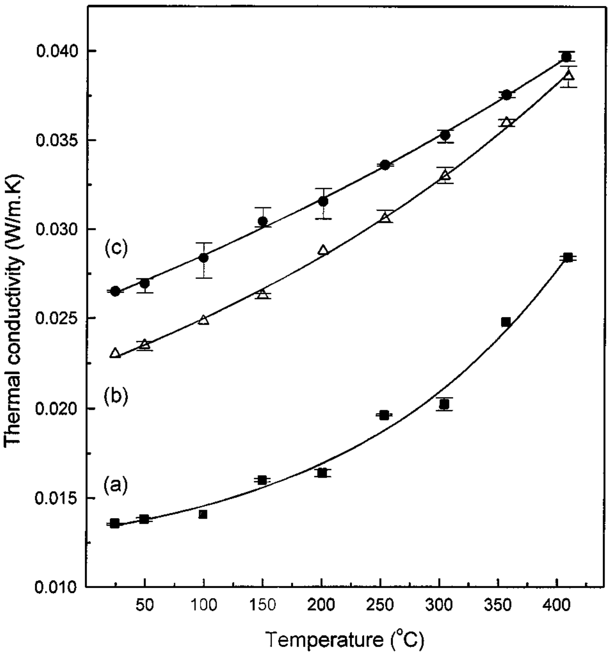

Figure 8 Thermal conductivities of aerogels as a function of temperatures; (a) 5STA heat-treated at 350°C, (b) pure silica aerogel heat-treated at 800°C, (c) 5STA heat-treated at 800°C.

Measurement was executed on pure silica aerogel heat-treated at 800 °C (density = 0.24 g/cm^3; sample A), 5STA heat-treated at 350 °C (density = 0.14 g/cm^3; sample B) and 5STA heat-treated at 800 °C (density = 0.27 g/cm^3; sample C). Fig. 8 shows that the thermal conductivity of aerogels in air increases with increasing temperature. The thermal conductivity of sample B (0.0136 W/m·K) remains lower than that of sample C (0.0256 W/m·K) because of lower density.

The radiative thermal conductivity of aerogels is strongly dependent on temperature. As shown in Fig. 8, the radiative thermal conductivity increases rapidly with temperature. The total thermal conductivity of samples C increases more quickly than that of sample A when the temperature increases up to 400 °C from the slope of the curves. The curve of sample A could be explained by the transparency of pure silica aerogel regarding thermal infrared radiation. The characteristic of pure silica aerogel is the low absorption region below 8 μm, which is responsible for a strong increase in thermal conductivity at elevated temperature. According to Fig. 8 it can be deduced that opacification of aerogel is highly effective to reduce the thermal conductivity of aerogel at elevated temperature. Therefore ambient-dried 5STA is clearly identified as high-quality alternative of thermal insulation allowing cheaper approach to synthesize aerogels.

4. Conclusion

Silica wet gel doped with 5 wt% TiO_2 powder was formed using two-step acid/base catalyzed SiO_2 sol by adding TiO_2 powder dissolved in ethanol. After surface modification by TMCS, SiO_2-5 wt% TiO_2 aerogel (5STA) was synthesized through drying and heat treatment at ambient pressure. When the heating temperatures was varied up to 1000 °C, apparent density lay between 0.14–0.47 g/cm^3 and corresponding porosity between 94–80%. Porosity and specific surface area tended to increase with the increase of heating temperature up to 350 °C, which is attributed to the spring back phenomenon that exhibits the swelling of the gel by means of the pressure of thermally expanded gases inside gel network pores during heat treatment and weight loss resulting from oxidation of organic groups in the gel. The thermal conductivity of 5STA heat-treated at 350 °C showed the lowest value of 0.0136 W/m·K at room temperature. In spite of higher density, the thermal conductivity of 5STA heated at 800 °C was similar to that of pure silica aerogel heated at 800 °C by reducing the radiative thermal conductivity resulting from opacification.

Acknowledgement

This work was supported by Keumkang Chemical Co. and Agency for Defense Development (ADD). The authors gratefully acknowledge the assistant of Dr. Seong, D. J. of Korea Research Institute of Standards and Science (KRISS) in the measurement of thermal conductivity.

References

1. J. FRICKE and T. TILLOTSON, *Thin Solid Films* **297** (1997) 212.
2. J. KUHN, T. GLEISSNER, M. C. ARDUINI-SCHUSTER, S. KORDER and J. FRICKE, *J. Non-Cryst. Solids* **186** (1995) 291.
3. D. J. KIM and S. H. HYUN, *J. Kor. Ceram. Soc.* **33**(5) (1996) 485.
4. D. M. SMITH, R. DESHPANDE and C. J. BRINKER, *Mat. Res. Soc. Symp. Proc.* **271** (1992) 567.
5. S. K. KANG and S. Y. CHOI, *J. Kor. Ceram. Soc.* **33**(12) (1996) 1394.
6. H. S. YANG and S. Y. CHOI, *ibid.* **34**(2) (1997) 188.
7. H. S. YANG, S. Y. CHOI, S. H. HYUN, H. H. PARK and J. K. HONG, *J. Non-Cryst. Solids* **221** (1997) 151.
8. S. K. KANG and S. Y. CHOI, *J. Mat. Sci.*, submitted.
9. H. S. YANG, S. Y. CHOI, S. H. HYUN and C. G. PARK, *Thin Solid Films* **348** (1999) 69.
10. Y. G. KWON, S. Y. CHOI and S. K. KANG, *J. Kor. Ceram. Soc.* **36**(11) (1999) 1189.
11. S. LOWELL and J. E. SHIELDS, "Powder Surface Area and Porosity" (Chapman & Hall, 1991) p. 52.
12. H. B. EBERT, V. BOCK, O. NILSSON and J. FRICKE, *High Temp.-High Press.* **25** (1993) 113.
13. R. K. ILER, "The Chemistry of Silica" (John Wiley & Sons, Inc., 1979) p. 622.
14. Z. DENG, J. WANG, A. WU, J. SHEN and B. ZHOU, *J. Non-Cryst. Solids* **225** (1998) 101.

Received 28 December 1999
and accepted 2 March 2000