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Ambient-pressure drying synthesis of high-performance silica aerogel powders by controlling hydrolysis reaction of water glass

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Silica aerogel powders were synthesized from inexpensive water glass under ambient-pressure drying (APD). Silica sol was synthesized by using adding hydrochloric acid (HCl) to diluted water glass, the silica sol was rapidly formed hydrogel by the addition of isopropyl alcohol (IPA), a new gelation agent. After solvent exchange and surface modification, silica aerogel powders were obtained by ambient-pressure drying the chemically treated hydrogel. This study especially investigates how the amount of added HCl affects properties of the silica aerogel powders, namely the tap density, specific surface area, pore size and volume, microstructure, and hydrophobicity. The aerogel powders size and density were found to decrease and the specific surface area, pore size and pore volume increase with increasing amounts of added HCl. The aerogel powders synthesized with the largest amount of HCl (volume ratio of HCl to water glass: 0.53) showed the tap density, specific surface area, pore size, pore volume, and thermal conductivity of 0.10 g/cm³, 819 m²/g, 12.00 nm, 3.14 cm³/g, and 0.023 W/mK, respectively. Also, it showed good hydrophobicity and thermal stability. It was evident that HCl addition amount can be one of key parameters to control the physical and thermal properties of silica aerogel.

Key words: Aerogel, Inorganic acid, Alcohol, Water glass, Ambient-pressure drying.

Introduction

Silica aerogels have become very popular in the field of materials because of their attractive properties such as low bulk densities (< 0.15 g/cm^3), high specific surface areas (> $500 \text{ m}^2/\text{g}$), high porosity (> 90%), and low thermal conductivities (~0.02 W/mK). The high porosity, high lightweight, and hydrophobicity of aerogels make them excellent thermal insulation, sound-absorbing, and heat shielding materials for building, industrial, ship construction, and aerospace applications [1-4].

The first synthesis of silica aerogels was performed by Kistler in 1931, using sodium silicate as a starting material through supercritical drying process. In the 1970s, a new process was developed by Techner to prepare silica aerogels within a day, by high-temperature supercritical drying of hydrogels obtained by hydrolysis of alkoxy precursors such as tetramethoxysilane (TMOS) in methanol solutions [5]. In 1983, Hunt and Berkeley Lab optimized this method by replacing the expensive and toxic TMOS with tetraethoxysilane (TEOS), and substituting the alcohol in the hydrogel with low-

temperature supercritical CO_2 [6]. However, the use of costly alkoxy precursors as starting materials and highcost supercritical drying make this process uneconomical. To solve this problem, Brinker et al. developed an APD process by exchanging the solvent and chemically modifying the hydrogel before drying [7, 8]. Generally, surface modification is performed after exchanging the water inside the hydrogel with another organic solvent that has weak surface tension, followed by modifying the hydrogel -OH group with silane group since the former causes condensation reaction on the hydrogel surface during drying and the latter is non-reactive [9-11]. Recently, it has been reported that trimethylchlorosilane (TMCS), IPA, and n-hexane are used to perform simultaneous surface modification and solvent exchange [12, 13], greatly shortening the processing time.

This study reports a new synthesis method of silica aerogel powders synthesized by using IPA as gelation material for obtaining hydrogel from silica sol which were synthesized by adding HCl to the diluted water glass and then using IPA to induce gelation. The synthesis of silica aerogel powders synthesized by using IPA as gelation material has not been reported in detail in the literature until now. Generally, a basic catalyst such as ammonium hydroxide (NH₄OH) is added to control the pH of silica sol to induce gelation [14-16]. Furthermore, the effects of different amounts

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of HCl on the aerogel properties were examined, while using the same amounts of diluted water glass, IPA as gelation material, exchange solvent, surface modifier, and APD conditions. The physical properties of the obtained silica aerogel powders such as tap density, specific surface area, pore size and pore volume, microstructure and hydrophobicity were investigated as functions of the amount of added HCl.

Experimental

Materials

Water-glass, i.e., sodium silicate (29 wt% SiO₂, Young II Chemical Co.), was used as a starting material for silica sol synthesis. The water-glass used in the experiment is an alkaline solution (pH = 11.5) containing 29 wt% SiO₂, 9 wt% Na₂O, and a small amount of Fe₂O₃ and has a viscosity (cPs > 100). HCl (1N, Samchun Chemical Co.) was used as catalyst for preparing silica sol from the diluted water glass and also for accelerating of hydrolysis and polycondensation reaction in silica sol. IPA (99.5%, Samchun Chemical Co.) was used as gelation material to form rapidly hydrogel by gelation from silica sol. *n*-Hexane (95.0%, Samchun chemical Co.) and TMCS (Samchun Chemical Co.) were used as exchange solvent and surface modifier, respectively.

Synthesis

Fig. 1 shows the flow chart of the new method of silica aerogel powders synthesized by ambient-pressure drying hydrogel, which synthesized by using IPA for gelation of the silica sol. To synthesize silica aerogel powders, silica hydrogel was synthesized from water glass (Na₂O:SiO₂ = 1:3.3) via a hydrolysis and polycondensation method, and then made hydrophobic by solvent exchange and surface modification followed by APD. Due to the



Fig. 1. Overall flowchart for the synthesis of water glass based silica aerogel powders.

high viscosity of water glass, it was diluted to suitable concentration (4.35 wt% SiO₂), and HCl was added to the diluted solution to prepare silica sol containing silanol (Si-OH) groups by hydrolysis reaction as shown in the below equation [17]. Then, silica hydrogel bonding siloxane (Si-O-Si) groups was formed by inducing polycondensation by adding IPA.

$$Na_2SiO_3 + 2HCl + (n-1)H_2O \rightarrow 2NaCl + SiO_2 \cdot nH_2O$$
(1)

In this study, silica aerogel powders were synthesized using different amounts of HCl in the sol formation step, with other experimental parameters kept constant. Specifically, 25, 27, 30, and 32 mL of HCl were added to 60 mL of diluted water glass (corresponding to HCl:water glass volume ratios of 0.42, 0.45, 0.50, and 0.53, respectively) to form silica sol. Further adding IPA (60 mL) to the silica sol formed hydrogel, which gelation takes place within 10 seconds. Subsequently, n-hexane and TMCS (volume ratios of 0.75 and 0.25 based on 60 mL of water glass) were simultaneously added to perform solvent exchange and surface modification, respectively, formed hydrophobic gel after 3-5 hrs chemical reaction with hydrogel by agitating the mixed solution containing silane agents and solvent. The gel was dried at 70 °C for 1 hr and then at 150 °C for 2-3 hrs under APD to afford silica aerogel powders.

Characterization

The microstructures of silica sol, hydrogel, and silica aerogel powders were observed by Field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi Co., Japan), and the corresponding textural properties were investigated by a Surface area analyzer (TriStar II 3020, USA) using the standard N_2 adsorption method. Silica aerogel powders were degassed at 573 K for 3 hrs, and adsorption-desorption isotherms were recorded at 77 K. Specific surface areas were calculated using the standard Brunauer-Emmett-Teller (BET) method, and cumulative pore volumes (V_c) were calculated from the N₂ adsorption-desorption profiles. The average pore diameters $(P_{\rm d})$ and pore size distributions (PSDs) were estimated using the Barrett-Joyner-Halenda (BJH) method. The tapping density of silica aerogel powders was calculated from its mass-to-volume ratio by using Multi Tester (MT-1001, Seishin Co., Japan). The thermal conductivities of silica aerogel powders were measured by means of heat flow method (HC-074, ECO Co., Japan).

The hydrophobicity of the silica aerogel powders was investigated by means of Fourier transform infrared spectroscopy (FT-IR, Nicolet 6700, Thermo, USA). Differential scanning calorimetry (DSC, Mettler Toledo Co.) was used to observe the oxidation or decomposition temperature of silane group ((Si-CH₃)₃) attached to the aerogel surface, with measurements performed between 0 and 600 °C at a heating rate of 10 °C/min. Ambient-pressure drying synthesis of high-performance silica aerogel powders by controlling hydrolysis reaction of water glass

Results and Discussion

Microstructure characterization

Fig. 2 shows the FE-SEM images of silica sol and hydrogel formed during the synthesis of silica aerogel powders. Specifically, Fig. 2(a) shows colloidal silica prepared by hydrolysis of water glass by adding 1 N HCl volume ratios of 0.42 to 0.50 to form silica sol. Fig. 2(b) represent hydrogels formed by adding IPA to silica sol to induce gelation, showing the presence of three-dimensional network structure considerably. In the SEM image of Fig. 2(a) and 2(b), the colloidal silica were smaller, and their aggregation was more prominent when the added HCl volume ratio was increased from 0.42 to 0.50.

Shown in Fig. 3, it is presumed that adding IPA to silica sol resulted in extensive hydrogen bonding between oxygen of –OH of IPA and hydrogen of –OH of water, which disrupted physicochemical bonding interactions between the silica particle surface (Si-OH) and surrounding water molecules [18, 19], causing gelation by instantaneous polycondensation.

Fig. 4 show that increasing the amount of HCl also produced smaller sizes and more aggregated microstructures



Fig. 2. SEM images of samples prepared with different ratios of 1N HCl/diluted water glass (0.42 and 0.50): (a) silica sol and (b) hydrogel.



Fig. 4. SEM image of silica aerogel powders synthesized with different ratios of 1N HCl/diluted water glass: (a) 0.42, (b) 0.45, (c) 0.50, and (d) 0.53.

in the silica aerogel powders [20]. This confirms that the amount of added HCl greatly influences the size and shape, microstructure of silica aerogel powders.

Physical property characterization

Increasing the HCl volume ratio from 0.42 to 0.53, the tap density decreased from 0.12 to 0.10 g/cm³. This decrease in tap density was attributed to the fact that HCl strongly affects the size and shape of powders, specific surface area and sizes and volumes of pore formed during the hydrolysis and polycondensation reactions of silica sol [21-23].

Fig. 5 shows the N_2 adsorption-desorption hysteresis loop of silica aerogel powders obtained with HCl volume ratios of 0.42, 0.45, 0.50 and 0.53. Their loop for silica aerogel powders could be categorized as type IV, corresponding to a mesoporous structure. The adsorption-desorption isotherms show that the volume of N_2 adsorbed per unit aerogel mass increased with increasing amount of added HCl amount, which increased the mesopore volume [24].

Fig. 6 shows the measured pore distribution for the silica aerogel powder. Most of the pores are 10 nm or less with a broad pore distribution. Fig. 5 and 6



Fig. 3. Gelation mechanism when IPA is added to 1N HCl/diluted water glass.



Fig. 5. Isotherms of the silica aerogel powders synthesized with different ratios of 1N HCl/diluted water glass.



Fig. 6. Pore size distributions of silica aerogel powders synthesized with different ratios of 1N HCl/diluted water glass.

illustrate that relatively smaller powders size and larger mesopore volumes were observed at HCl volume ratios of 0.50 and 0.53, resulting in enhanced N₂ adsorption. In particular, relatively high amounts of micropores in the silica aerogel powders were observed at the HCl volume ratio of 0.53. On the other hand, relatively low amounts of N₂ adsorption were observed at volume ratios of 0.42 and 0.45, due to the increased powders size and smaller mesopore volume.

Fig. 7 plots the specific surface area vs. pore size, and pore volume vs. pore size with different amount of added HCl. As the amount of HCl increases, all three



Fig. 7. Correlations of physical properties of silica aerogel powders synthesized with different ratios of 1N HCl/diluted water glass: (a) BET specific surface area vs. average pore diameter, (b) average pore volume vs. pore diameter.

values tend to increase. Thus, at HCl volume fractions of 0.42 and 0.45, the specific surface areas ($\leq 451 \text{ m}^2/\text{g}$), pore sizes (≤ 10.00 nm), and pore volumes (≤ 0.82 cm³/ g) of silica aerogel powders were represented low value of the properties. On the other hand, at volume ratios of 0.50 and 0.53, the specific surface area is \geq 715 m²/g, the pore size is ≥ 12.00 nm, and the pore volume is \geq 2.60 cm³/g. All three values generally increased with the amount of added HCl, except that the average pore diameter decreased at HCl volume fractions of 0.53, due to the presence of high amounts of micropores [25, 26]. Thus, the properties of silica aerogel powders were significantly influenced by the amount of added HCl, which affected the three-dimensional network structure via hydrolysis and polycondensation of solgel process.

Table 1 summarizes the tap densities, specific surface areas, and pore sizes and pore volumes, of the silica aerogel powders synthesized with different amounts of HCl. Increasing the HCl volume ratio from 0.42 to 0.53 decreased the tap density to $0.12-0.10 \text{ g/cm}^3$, and increased the specific surface area, pore size and pore volume of silica aerogel powders. The pore size of silica aerogel powders first increased with increasing HCl volume ratio up to 0.50, and then decreased to 0.53. The silica aerogel powders synthesized with the largest amount of HCl (volume ratio: 0.53) showed the tap density, specific surface area, pore size and volume, and thermal conductivity of 0.10 g/cm³, 819 m²/g, 12.00 nm, 3.14 cm³/g, and 0.023 W/mK, respectively, showing its good physical and thermal properties. Especially, the small thermal conductivity means that HCl addition is one of key parameters to control the properties of silica aerogel.

Table 1	 Physical 	and thermal	properties	of silica	aerogel	powders.
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Sample	No. added Acid value	Tapping density (g/cm ³)	Surface Area (m ² /g)	BJH V _C (cm ³ /g)	BJH P _d (nm)	Thermal conductivity (W/mK)
	0.42	0.12	345	0.41	7.87	
Silica aerogel powders	0.45	0.11	451	0.82	9.71	
	0.50	0.11	715	2.61	13.81	
	0.53	0.10	819	3.14	12.00	0.023

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FT-IR and DSC analyses

Fig. 8 shows FT-IR spectra of silica aerogel powders obtained with HCl volume ratios of 0.42, 0.45, 0.50, and 0.53, revealing the presence of Si-O-Si peaks at 1080 cm⁻¹ in all cases. Peaks of Si-(CH₃)₃ groups observed at 750, 850, 1255, and 2975 cm⁻¹ [27] indicated that the Si-OH groups initially present on the silica surface were converted to Si-O-Si-(CH₃)₃ groups, rendering the surface hydrophobic.

Fig. 9 shows the DSC curves of hydrophobic silica aerogel powders, revealing a significant exothermic peak at around 400-490 °C attributed to the oxidation or decomposition of Si-(CH₃)₃ groups on the surface of silica [28, 29]. This peak means the temperature at which the silica surface changes from hydrophobic to hydrophilic, and the peak position shifts to higher temperatures when less amount of HCl is added. This result related to the fact that the amount of TMCS added during process of surface modification was constant in these experiments, whereas adding more



Fig. 8. FT-IR spectra of hydrophobic silica aerogel powders synthesized with different ratios of 1N HCl/diluted water glass: (a) 0.42, (b) 0.45, (C) 0.50, and (d) 0.53.



Fig. 9. DSC curves of silica aerogel powders synthesized with different ratios of 1N HCl/diluted water glass: (a) 0.42, (b) 0.45, (C) 0.50, and (d) 0.53.



Fig. 10. Hydrophobicity test of silica aerogel powders synthesized with different ratios of 1N HCl/diluted water glass, after heat-treating the silica aerogel powders at 450 °C for 1hr: (a) initial state and (b) after 6 hrs in water.

amount of HCl increased the specific surface areas of silica aerogel powders. Hence, a higher amount of added HCl lowered the areal density of hydrophobic Si-(CH₃)₃ groups of silica aerogel powders surface, allowing the hydrophobic-to-hydrophilic transition to occur at lower temperatures.

The other test on the loss of hydrophobicity of the silica aerogel materials had been reported as follows. After the silica aerogel powders were heated in a furnace at expected transition temperature, placed in a beaker filled with water, and then kept there, resulting in silica aerogel powders precipitation due to the loss of hydrophobicity [30]. Based on the above DSC results, the synthesized silica aerogel powders were heated in a furnace at 450 °C for 1 hr, placed in a beaker filled with water, and kept there for 6 hrs. Fig. 10 show that the samples synthesized using HCl volume ratios of 0.42 and 0.45 float on the surface of water. In contrast, those obtained using volume ratios of 0.50 and 0.53 only partially precipitated, and the rest remained on the surface of water. These results revealed that silica aerogel powders synthesized using different amounts of HCl maintain hydrophobicity in this temperature range from 400 to 490 °C. This test is in agreement with the DSC results.

Conclusions

In the present study, high performance silica aerogel powder was synthesized by controlling the volume ratio of added HCl during silica sol formation from water glass. Increasing the volume ratio of added HCl during synthesis process, the specific surface areas and pore size and volume of the synthesized silica aerogel powders increased, and the corresponding tap densities decreased. These silica aerogel powders showed the tap density, specific surface area, pore size, pore volume, and thermal conductivity of 0.10 g/cm³, 819 m²/g, 12.00 nm, 3.14 cm³/g, and 0.023 W/mK, respectively, showing its good physical and thermal properties. Also, the synthesized silica aerogel powders maintained the hydrophobicity in the temperature range of 400 to 490 °C. These results revealed that HCl addition is one of key parameters to control properties of silica aerogels synthesized from water glass.

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