Thermal Properties of Monolithic Silica and Silica–Zirconia with Bimodal Pore Structures

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二元細孔シリカ及びシリカ−ジルコニアの熱的特性
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Thermal properties of bimodal porous silica and silica–zirconia with humidity control ability are investigated in order to clarify their potential as a multi-functional building material. Thermal conductivity of the silica decreases with increasing the porosity of the silica, and 0.06 W m⁻¹K⁻¹ is achieved when the porosity exceeds 90%. The silica shows thermal resistance of ca. 800°C, which is much higher than conventional thermal insulators. The thermal resistance can be improved by the addition of zirconia: a silica–zirconia sample maintains its high porosity up to 1050°C. Thus, the bimodal porous silica and silica-zirconia are expected to be a thermal insulator with humidity control and thermal resistance abilities.

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1. Introduction

A bimodal porosity with macropores and mesopores is effective to improve the ability of porous materials through the enhancement of molecular transportation in the materials. Silica gels prepared from silicon alkoxides⁴⁻⁶ and water glass⁷,⁸ by fixing transitional structures of phase separation have typical bimodal porosity. They have three-dimensionally bi-continuous morphology of pores and silica gel skeleton in micrometer scale, and mesopores exist in the silica skeleton. The macropores can be pathways for rapid diffusion and mass flow to access the functionalized mesopores.⁹⁻¹¹ In addition, the bimodal porous silica has much higher porosity than conventional silica gels. For example, porosity of commercial silica gels for catalyst supports and adsorbents is ca. 70% as the highest,¹² whereas the bimodal porous silica has typical porosity of ca. 90%.¹³ This high porosity of bimodal porous silica is comparable with that of silica aerogel with high thermal insulation ability.¹⁴ Then, we can also expect the bimodal porous silica as a thermal insulator.

In our previous work, we have shown that the bimodal porous silica prepared from water glass has excellent character as a humidity control material from both equilibrium and kinetic aspects.¹⁵ Water glass is an industrial raw material of silica gel, and we can prepare the silica from water glass with much lower cost than preparing from silicon alkoxides. Therefore, the water-glass-derived bimodal porous silica is suitable in use as a building material for humidity control. In buildings, high thermal insulation is also required, and glass wool and/or polymer foam are widely used as a thermal insulator.¹⁶ Recently, a thermal insulator with humidity control ability attracts much attention because of its potential in passive control of air condition and to inhibit dew condensation within the thermal insulator.¹⁷

We now propose that the water-glass-derived bimodal porous silica can be a thermal insulator with humidity control ability. Such multi-functionality is required to a newly developed material in the term of synergy. The silica has another advantage. Silica has high thermal stability compared to conventional thermal insulators made with glass wool and/or polymer foam.¹² Furthermore, various characters of silica-based glasses and gels, such as fracture toughness, alkali resistance, steam resistance and thermal stability, can be improved by the addition of zirconia.¹⁷⁻²³ Therefore, further improvement of the thermal stability would be possible.

In this work, we aimed to clarify the thermal properties of the bimodal porous silica. We investigated some properties of the silica samples, such as thermal conductivity, thermal stability, and strength, in order to evaluate their potential as multi-functional building material. In addition, we improved the thermal stability of the silica by adding zirconia.

2. Experimental

2.1 Sample preparation

Bimodal porous silica gels were prepared from water glass (JIS No. 3 water glass containing 29 mass%SiO₂ and 10 mass%Na₂O, Tokuyama Co.) in the presence of Poly (acrylic acid) (HPAA) with an average molecular weight of 25000 (Wako Pure Chemicals Industries), according to the method reported previously.⁷,¹³ Starting compositions were water glass: water: HNO₃ (60 mass% aqueous solution) : HPAA = x : 97 : 3 : 6.5 in weight ratio, where x varied from 50 to 60. All wet gels obtained by gelation at 25°C were aged in 1 mol dm⁻³ ammonia aqueous solution at 50°C for 3 days, then dried at 50°C until no shrinkage was observed. The dry gels were calcined at the prescribed temperature between 500 and 1400°C for 2 h with heating rate of 100°C h⁻¹. Some dry gels were immersed in a zirconyl nitrate solution with an appropriate concentration in order to load zirconia, and re-dried at 50°C before calcination. A silica gel sample without macropores for comparison was prepared from tetraethyl orthosilicate (TEOS) as reported elsewhere.²⁴ Aging, drying and calcination were adopted with the same conditions as the bimodal porous silica.
2.2 Characterization

Scanning electron microscope (SEM, SM2000, Topcon) was employed for the observation of micrometer-scale morphology of the bimodal porous samples. A nitrogen adsorption isotherm was measured at −196°C using OMNISORP 100CX (Beckman Coulter) after the sample had been degassed at 300°C for 1 h. The specific surface area, \( A \), and mesopore volume, \( V_{\text{meso}} \), were calculated from the adsorption isotherm by the BET method and the amount of \( N_2 \) adsorbed at \( P/P_0 > 0.95 \), respectively. Total pore volume, \( V_t \), including both mesopores and macropores was calculated from the difference in weight between the sample dried at 110°C and the sample containing water fully in its pores together with density of water. The porosity of the silica gel, \( \phi \), was calculated by the following equation assuming that the density of silica, \( d \), is 2.20 g cm\(^{-3}\).

\[
\phi = \frac{V_t}{V_t + d^{-1}}
\]

X-ray diffraction (XRD) patterns were recorded on an M18XHF (Mac Science) using Cu Kα radiation (\( \lambda = 0.154 \) nm) to detect the crystal structure of the samples. Thermal conductivity of the monolithic silica gels was measured by the hot-disk method (TPA-501, Kyoto Electronics). Bending strength was measured on SV-55C-5M (Imada) by 3-point bending test according to JIS R 1061 using test pieces with dimensions of 3.4*40 mm. Zirconia content in the samples with zirconia was detected with inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICPS-8100, Shimadzu).

3. Results

Figure 1 shows the SEM images of fractured surfaces of silica gels. All the samples prepared with different composition and calcined at 800°C show bicontinuous morphology, while the size of pores increases with increasing water glass content as reported previously.\(^7\) The bicontinuous morphology is retained up to ca. 1100°C, although decrease in pore size is recognized over 800°C. Over 1100°C, macropores almost collapse due to deformation of pores. Figure 2 shows the change in morphology of silica-zirconia with calcination temperature. The zirconia content was ensured to be 4 mass% by the ICP measurement. In contrast to the pure silica gel, shrink in pore size is not observed below 1000°C. Although the size of pores becomes small, bicontinuous morphology is maintained up to 1300°C. Deformation of pores is observed at 1400°C.

Figure 3 shows the change in porosity of the samples with calcination temperature. All the silica samples keep high porosity between 80 and 90% up to 800°C. Porosity decreases gradually over 850°C, and steeply around 1000°C. Among the pure silica samples, a sample with small macropores (open circle) shows higher porosity than those with large macropores. The porosity of silica-zirconia decreases over 1050°C, about 200°C higher than pure silica.

In the samples, both macropores as observed with SEM and mesopores located in the gel skeleton contribute to the porosity. Then, we further investigate the change in the mesoscale structure with calcination temperature to see the stability of mesopores and macropores separately. Figures 4 and 5 show the changes in pore volume and specific surface area with calcination temperature, respectively. The change in total pore volume shows a trend similar to the porosity as obvious from Eq. (1). The mesopores and specific surface area also change with similar manner to porosity, but they disappear about 200°C lower temperature than the temperature at which porosity becomes almost zero. Thus, both mesopores and macropores decrease their volume between 800 and 1000°C in
the silica. It would be said that the silica gel shrinks isotropically so that the ratio between macropore volume and the sum of silica gel and mesopore volumes does not change so much. This scheme well corresponds the morphology change observed with SEM (Fig. 1): morphology does not change except for the size below 1100°C. Over 1100°C, mesopores disappear, while macropore volume becomes small due to collapse of macropores by the change in morphology. In the silica–zirconia, these changes occur at higher temperatures by about 200°C. Comparing with pure silica, it is clear that thermal stability is improved about 200°C by the addition of zirconia. We prepared two samples with different zirconia content, 4 and 7 mass%, while there is little difference in pore structure evolution between the two samples.

**Figure 6** shows the change in XRD profiles with calcination temperature. Crystallization of cristobalite was observed at 1200 and 1400°C for pure silica and silica–zirconia, respectively. In addition, diffraction peaks of tetragonal zirconia are observed together with broad halo of amorphous silica in the silica–zirconia sample at <1300°C.

**Figure 7** shows the relation between thermal conductivity and porosity of bimodal porous silica gel. Thermal conductivity of silica glass is ca. 1.5 W m⁻¹K⁻¹. As expected, thermal conductivity decreases with increasing porosity of the silica gel. The silica without macropores has low porosity, and as a result, it shows high thermal conductivity. The minimum value measured is ca. 0.06 W m⁻¹K⁻¹ at 92% porosity.

In the preliminary strength test by adopting 3-point bending method, we obtain the bending strength of 2.1 and 2.7 MPa for silica and silica–zirconia samples calcined at 800°C, respectively. Although these values are much smaller than the strength of pure silica glass, 107 MPa, they are reasonable by taking into account the high porosity of these materials. The addition of zirconia seems to increase the strength of the silica, but strength is also a function of porosity. Further investigation is necessary to clarify how structural and compositional parameters affect the strength of the bimodal porous materials.
4. Discussion

4.1 Effect of the addition of zirconia on the thermal stability

During heating, a porous material tends to decrease its surface area in order to lower the surface energy. In the present silica, mesopore volume and specific surface area began to decrease over 850°C. That is, the silica has thermal stability up to 850°C. This seems to be somewhat lower than TEOS-derived gel used as catalysts,\textsuperscript{26} while comparable with water-glass-derived gels.\textsuperscript{12} Residual soda comes from water glass would be an origin of it. The decrease in the porosity below 1100°C mainly occurs due to the shrinkage of mesopores, which induces isotropic shrinkage of gel body. The decrease in porosity over 1100°C is attributed to the collapse of macropores due to the deformation of morphology. This deformation temperature is comparable to the data reported for TEOS-derived gel.\textsuperscript{23} Part of silanols on sol-gel-derived silica gel would remain in the silica network after disappearance of mesopores. Breakage of Si-O-Si bonds due to OH groups decreases thermal stability of silica gel. Viscous flow of silica skeleton with an appropriate amount of OH would be an origin of this deformation. Crystallization of cristobalite concurrently occurs due to the effect of residual sodium and/or the increase in mobility of silica network.

Thermal stability of the silica was improved by the addition of zirconia: the temperatures, at which structural changes of bimodal silica occur, shift to 200°C higher side. As described above, the addition of zirconia in silica-based glass has an effect to improve various characters including thermal stability.\textsuperscript{17–23} Because the added zirconia is present as tetragonal crystals rather than being incorporated in silica network in atomic level, the improvement of the thermal stability would not be caused by the atomic-level-mixing of Zr in silica network. Such small crystals may work as obstacles to prevent viscous flow of amorphous silica matrix, or crystallization of zirconia in amorphous silica would have an effect to decrease OH content in the silica network for some mean. Crystallization temperature of cristobalite also increases from 1200 to 1400°C. Crystallization and deformation of macropores occur simultaneously for both silica and silica–zirconia samples, although the crystallization temperature differs about 200°C. Crystallization of cristobalite requires reconstruction of silica network. Therefore, it is reasonable to consider that the amount of residual OH in the silica network plays an important role in the thermal stability and crystallization. However, the origin of the effect of the addition of zirconia should be further investigated.

4.2 Potential as a multifunctional building material

We investigated to propose that the bimodal porous silica gel prepared from water glass could be a multi-functional building material with humidity control, thermal insulation and thermal resistance. As demonstrated in the previous work, the bimodal silica showed excellent characters in humidity control.\textsuperscript{13} It shows high adsorption capacity and high adsorption rate of water vapor. The humidity at which reversible adsorption-desorption cycle occurs is easily controlled by changing mesopore size.

In the thermal insulation, we obtained the thermal conductivity of 0.06 W m\(^{-1}\) K\(^{-1}\) at 92% porosity, as the minimum in this work. A silica aerogel prepared by supercritical drying of sol-gel-derived silica gel has been well known to have very low thermal conductivity of 0.01 W m\(^{-1}\) K\(^{-1}\).\textsuperscript{14} The thermal conductivity of air at room temperature is ca. 0.03 W m\(^{-1}\) K\(^{-1}\), and usual thermal insulators composed of glass wool or organic polymer foam such as polyurethane have thermal conductivity of ca. 0.03–0.05 W m\(^{-1}\) K\(^{-1}\).\textsuperscript{15} The thermal conductivity of the present material is somewhat larger than that of these materials, but in the same order as these materials. Therefore, we expect that the bimodal porous silica can be a thermal insulator.

In addition, the bimodal porous silica has another advantage. A thermal insulator made with organic polymer is thermally unstable and sometimes becomes an origin of poisonous gases during fire. The wood-derived insulator with humidity control ability also burns during fire. Glass wool is not thermally stable, either: it easily melts over ca. 500°C. The bimodal porous silica has much higher thermal stability compared with them. The pore structures are maintained up to 800°C. Furthermore, we can increase the thermal stability of the material to 1050°C by adding zirconia. Because of this thermal stability, the bimodal porous silica can be used for fireproof. This improvement of thermal stability is easily achieved by the simple impregnation of silica gel in zirconyl nitrate solution. This is convenience in the material design because the effect of the addition of zirconia on the mesopore and macropore structures is little. Furthermore, increase in the stability against the repeated exposure to water vapor is also expected by the addition of zirconia as demonstrated for the improvement of stability against steam.\textsuperscript{21}

Thus, we can expect the bimodal porous silica with zirconia to have tri-function in the use as building materials: humidity control, thermal insulation, and thermal resistance.

5. Conclusion

Thermal properties of bimodal porous silica monolith is investigated from the viewpoint of application as a multi-functional building material. Thermal conductivity of the silica is controlled in the range between 0.06 and 0.09 W m\(^{-1}\) K\(^{-1}\) by changing the porosity of the silica between 92 and 83%. Thermal shrinkage of pore structures of the silica is observed over 800°C, and viscous flow of macroporous structure is observed over 1100°C. These thermal resistance properties are improved by the addition of zirconia to 1000 and 1300°C, respectively. In addition to the superior humidity-control ability reported previously, the bimodal porous silica is expected as a multi-functional building material with thermal insulation and thermal resistance.

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