A glass fiber cloth (GFC) with microporosity was prepared upon the suppression of crack generations. After the prepared GFC was heat-treated, it was slowly cooled to room temperature and then subsequently treated with hydrochloric acid. The experimental data through complementary techniques including scanning electron microscopy, nitrogen adsorption/desorption isotherm, solid-state $^{29}$Si nuclear magnetic resonance spectroscopy, and elemental analysis revealed the conversion of the slowly-cooled GFC into a microporous solid with no cracks in each glass fiber upon the alkaline leaching by hydrochloric acid. These results clearly indicated the formation of microporous GFC without cracking.

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Key-words : Glass fiber cloth, Porous solid, Silica, $^{29}$Si MAS NMR, Catalyst support

1. Introduction

Inorganic microporous solids, such as zeolites, have been widely investigated in various fields, including adsorption,\(^ {11} \) materials besides catalysts,\(^ {5,3} \) and their supports,\(^ {9} \) whose practical applications require inorganic microporous solids to be used in appropriate morphologies, such as bulk,\(^ {5,6} \) granule,\(^ {5,6} \) membrane,\(^ {7,8} \) and cloth\(^ {9,10} \) morphologies. Regarding cloth with flexible morphology, inorganic microporous solids can be supported on cloth.\(^ {9,10} \) A cloth can be also converted into a microporous solid through the micropore formation in each fiber knitted into the cloth; glass fiber cloth (GFC), which consists of electrically applied glass (E-glass) fibers that mainly comprise 56–62 SiO\(_2\), 16–25 CaO, 12–16 Al\(_2\)O\(_3\), 0–10 B\(_2\)O\(_3\), and 0–5 MgO in mass%, has been converted into microporous solids through an acid treatment to leach its alkaline contents.\(^ {11–14} \) Micrometer-range crack generations in each glass fiber were unavoidable, however.\(^ {12–14} \) As concerns glass fiber production processes, when glass fibers are spun, the thermal history of their surfaces differed from that of their inner cores, forming structural differences between the surface and inner fibers.\(^ {15,16} \) This leads to the formation of porous fiber surfaces and non-porous fiber inner surfaces upon GFC acid treatments,\(^ {12–14,17} \) resulting in the induction of tensile stresses in the porous surfaces, which can horizontally or vertically break the fibers.\(^ {12–14} \) Despite the above-mentioned crack generations, the acid-treated GFC, the microporous GFC achieved concentration of gas molecules in their micropores.\(^ {14} \) Additionally, the microporous GFC successfully acted as titania support.\(^ {14} \) Suppressing the crack generations of microporous GFC is thus challenging when it comes to realizing microporous GFC as a more reliable microporous solid.

Here, we report the preparation of microporous GFC without cracking. GFC and its products were cut using a dressmaking shear into appropriate sizes and sheets for each experiment and characterization. After the heat treatment and subsequent slow cooling of GFC, the obtained GFCs underwent acid treatments to form microporous GFCs. These procedures were mainly based on the obtained information in previous reports; the heat treatment of GFC at around its glass transition temperature with subsequent slow cooling canceled the structural differences between its fiber surfaces and inner cores, forming more homogeneous and dense structures, which showed lower alkaline content dissolution than that of untreated GFC upon the acidic treatment of GFC.\(^ {15,16} \) Since the obtained microporous GFCs exhibit no crack generations and the GFC porosities are changed with the acid treatment time, the micropore formation mechanism is clearly discussed using $^{29}$Si and $^1$H nuclear magnetic resonance (NMR) spectroscopy.

2. Experimental

2.1 Materials

GFC was obtained from Arisawa Manufacturing Co.
Ltd. (Joetsu Japan). Hydrochloric acid [HCl (aq.)] with a concentration of 5 mol/L, ethanol, hexamethylbenzene, and polydimethylsiloxane was obtained from Wako Pure Chemical Ind., Ltd. All the chemicals were used without further purification. The powder and liquid whose mixtures rapidly formed poly(methyl methacrylate) (PMMA) resin (Technovit 4004) were obtained from Kulzer Japan Co. Ltd.

2.2 Sample preparation
After the GFC was heat-treated at 700 °C for 6 h in an electrical furnace, the heat-treated GFC (h-GFC) was allowed to stand in an electrical furnace until it cooled to room temperature, forming the slowly-cooled h-GFC (sc-h-GFC). The sc-h-GFCs were placed in 5-mol/L HCl (aq.) (50 mL) at 95 °C for 0.5, 1, or 3 h in a sealed vessel, respectively. After the reactions, the resultant solids were removed from the resultant solutions using tweezers and then washed with an excess amount of distilled water and then with ethanol. Afterward, they were dried at 120 °C for 10 min (sc-h-GFC0.5 h, sc-h-GFC1 h, and sc-h-GFC3 h). After the preparation, the products were folded in half and were subsequently unfolded using tweezers.

2.3 Characterization
Scanning electron microscopy (SEM) images were obtained using a Hitachi TM-3000 microscope. Prior to the measurements, some samples were embedded in PMMA resin (see the materials section) and were then cut, and the cross-sections were polished appropriately. The nitrogen adsorption/desorption isotherms of the samples were measured at −196 °C using a Belsorp MINI instrument (MicrotracBEL Inc.). Prior to the measurements, the samples were dried at 120 °C under reduced pressure for 3 h. The surface areas of the samples were determined from the adsorption isotherms using the Brunauer–Emmett–Teller method for convenience. Elemental analyses were conducted using a wavelength-dispersive X-ray fluorescence spectrometer (Rigaku ZSX). The solid-state 29Si and 1H NMR spectra were recorded on a JEOL JNM CMX-400 spectrometer at 79.42 and 399.78 MHz, respectively. The solid-state 29Si NMR spectra were obtained using the magic angle spinning (MAS) technique with a pulse delay of 60 s. The solid-state 29Si NMR spectra were also obtained using cross-polarization (CP) and MAS techniques at a contact time of 5 ms. The solid-state 1H NMR spectra were obtained using MAS technique with a pulse delay of 5 s. The samples were put into a 5-mm zirconia rotor with a spinning rate of 8 kHz. The 29Si and 1H chemical shifts were externally referenced to polydimethylsiloxane at −33.8 ppm and hexamethylbenzene at 2.31 ppm, respectively.

3. Results
Not many differences were observed between the looks of the GFC and the products, indicating the preservation of cloth morphology. By contrast, sc-h-GFC0.5 h and sc-h-GFC3 h were hardly broken, whereas sc-h-GFC0.5 h was split in two upon the folding and subsequent unfolding using tweezers (Fig. 1).

Figure 2 shows SEM images of the products and their cross-sections. The image of sc-h-GFC [Fig. 2(a)] shows a fiber-like morphology, which is similar to those observed in previous studies. The image of sc-h-GFC is similar to the images of sc-h-GFC1 h and sc-h-GFC3 h [Figs. 2(c) and 2(d)], whereas the image of sc-h-GFC0.5 h displays a cracked fiber-like morphology [Fig. 2(b)]. Compared with the cross-section image of sc-h-GFC [Fig. 2(e)], the cross-section images of sc-h-GFC1 h and sc-h-GFC3 h exhibit stronger contrasts in a circle-like morphology [Figs. 2(g) and 2(h)]. They were, however, unlikely similar to the cross-section images of sc-h-GFC0.5 h [Fig. 2(f)], which shows high contrasts between the outer and inner parts in the circle-like morphology, which is similar to the case of the previously-reported GFCs that underwent acid treatments.

Figure 3 shows nitrogen adsorption/desorption isotherms of the products. The amounts of nitrogen of sc-h-GFC1 h and sc-h-GFC3 h are much larger than that of sc-h-GFC, and the amount of nitrogen of sc-h-GFC1 h is larger than that of sc-h-GFC3 h in all the P0/P range. In addition, nitrogen adsorption/desorption isotherms of sc-h-GFC1 h and sc-h-GFC3 h are typical I type, indicating the presence of micropores in the products. The surface areas of sc-h-GFC1 h and sc-h-GFC3 h are 545 and 461 m2/g, respectively.

Based on the performed elemental analyses, Na2O, MgO, Al2O3, and CaO, which were detected in sc-h-GFC, were hardly detected in sc-h-GFC1 h and sc-h-GFC3 h, whose detectable components were solely SiO2.

Figure 4 shows 29Si MAS NMR and 29Si CP/MAS NMR spectra of the products. As for 29Si MAS NMR spectra, in the spectrum of GFC, the broader signal is observed at around −94 ppm [Fig. 4(a)]. Compared with the spectrum of GFC, a similar broader sig-

![Fig. 1. Photographs of (a) sc-h-GFC0.5 h, (b) sc-h-GFC1 h, and (c) sc-h-GFC3 h after folding in half and subsequent unfolding by a tweezer.](image-url)
nal is observed in the spectrum of sc-h-GFC, whereas the position is at around $-95$ ppm [Fig. 4(b)]. The $-94$-ppm signal is thus slightly shifted to upfield by $-1$ ppm, a result well-consistent with the minute upfield shift of the signal due to slowly-cooled E-glass from that of fast-quenched E-glass by $-0.7$ ppm in the previous report.20) The possible reasons were as follows; 1) the relaxation of glass structures from Q3 to Q4 and Q2, and vice versa; 2) the change in the bond angles of Si–O–Si and/or Si–O–M (M represents network former components).21) The broader signal at $-95$ ppm observed in the spectrum of sc-h-GFC [Fig. 4(b)], meanwhile, disappears along with the appearance of new signals at $-97$, $-107$, and $-116$ ppm in the spectrum of sc-h-GFC\(._{1\text{h}}\) [Fig. 4(d)], whereas the relative intensities of the $-97$- and $-107$-ppm signals with respect to the $-116$-ppm signal decrease as compared to the signals observed in the spectrum of sc-GFC\(._{1\text{h}}\). Concerning $^{29}$Si CP/MAS NMR spectra, no signals are observed in the spectra of both GFC and sc-h-GFC [Figs. 4(a) and 4(b)], whereas $-97$, $-107$, and $-116$-ppm signals are observed in the spectra of both sc-GFC\(._{1\text{h}}\) and sc-h-GFC\(._{3\text{h}}\). With respect to the comparison between the $^{29}$Si MAS spectra and $^{29}$Si CP MAS NMR spectra, in the spectra of sc-h-GFC\(._{1\text{h}}\) and sc-h-GFC\(._{3\text{h}}\), the relative intensities of the $-97$- and $-107$-ppm signals with respect to the $-116$-ppm signal observed in the $^{29}$Si CP/MAS NMR spectra increase as compared to the signal intensities observed in the $^{29}$Si MAS NMR spectra.

Figure 5 shows $^1$H MAS NMR spectra of sc-h-GFC\(._{1\text{h}}\) and sc-h-GFC\(._{3\text{h}}\). The spectrum of sc-h-GFC\(._{1\text{h}}\) shows the 7- and 1.8-ppm shoulders and the 4- and 0.8-ppm signals, while that of sc-h-GFC\(._{3\text{h}}\) exhibits the 7-ppm shoulders and the 3.8-ppm signal.

Fig. 2. SEM images of (a) sc-h-GFC, (b) sc-h-GFC\(._{0.5\text{h}}\), (c) sc-h-GFC\(._{1\text{h}}\), (d) sc-h-GFC\(._{3\text{h}}\), (e) the cross-section of sc-h-GFC, (f) sc-h-GFC\(._{0.5\text{h}}\), (g) the cross-section of sc-h-GFC\(._{1\text{h}}\), and (h) the cross-section of sc-h-GFC\(._{3\text{h}}\).

Fig. 3. The nitrogen adsorption (open marks)/desorption (filled marks) isotherms of sc-h-GFC (square), sc-h-GFC\(._{1\text{h}}\) (circle), and sc-h-GFC\(._{3\text{h}}\) (triangle).

Fig. 4. $^{29}$Si MAS (solid line) and CP/MAS (dashed line) NMR spectra of (a) GFC, (b) sc-h-GFC, (c) sc-h-GFC\(._{1\text{h}}\), and (d) sc-h-GFC\(._{3\text{h}}\). Dotted lines are deconvolutional components.
4. Discussion

The closer looks at the GFC and the products, SEM images (Fig. 2), the I type nitrogen adsorption and desorption isotherms (Fig. 3), and elemental analyses reveal that the alkaline leaching of sc-h-GFC successfully proceeds from the glass fiber surfaces to the inners in the 0.5–1 h range by the acid treatment to convert sc-h-GFC into silica-based microporous solids upon the suppression of crack generation where the tensile stresses due to the silica-based microporous solids upon the suppression of crack generation to convert sc-h-GFC into amorphous silica-like amorphous solids, which have showed vast various pore environments with appropriate deconvolutions as shown in dotted lines in Figs. 4(c) and 4(d), respectively (the ratios of Q2 and Q3 per Q4 [(Q2 + Q3)/Q4] of sc-h-GFC.1 h and sc-h-GFC.3 h are, therefore, estimated at 1.0 and 0.84 using their 29Si signal integrals with appropriate deconvolutions as shown in dotted lines in Figs. 4(c) and 4(d), respectively (the ratios of Q2:Q3:Q4 are 1:14:15 for sc-h-GFC.1 h and 1:20:25 for sc-GFC.3 h). The Q2 and Q3 environments observed in the sc-h-GFC.3 h thus decrease from those observed in the sc-h-GFC.1 h. Regarding the 1H MAS NMR spectra, signals observed in spectra of sc-h-GFC.1 h and sc-h-GFC.3 h (Fig. 5) are assignable as follows; 1) the 7-ppm shoulder is assignable to adsorbed water;24) 2) the 4-ppm signal observed in the spectrum of sc-h-GFC.1 h is the hydrogen-bonded silanol groups;25) 3) the 0.5-ppm signal and the 1.8-ppm shoulder are assignable to isolated silanol groups.23) The 1H signal integrals with appropriate deconvolutions as shown in dotted lines in Fig. 5, the silanol group contents of sc-h-GFC.1 h and sc-h-GFC.3 h are estimated at 48 and 30 mmol/g, respectively.

The present mechanism of the micropore formations is as follows. Based on the 29Si and 1H MAS NMR spectra, the ratios of Q2 and Q3 per Q4 [(Q2 + Q3)/Q4], elemental analyses, and 1 type-nitrogen adsorption/desorption isotherms, the silanol groups form in sc-h-GFC upon its alkaline leaching by HCl (aq.) to generate micropores in the glass fiber surfaces to the inners in the 0.5–1 h range by the acid treatment to convert sc-h-GFC into silica-based microporous solids upon the suppression of crack generation where the tensile stresses due to the silica-based microporous solids upon the suppression of crack generation to convert sc-h-GFC into amorphous silica-like amorphous solids, which have showed vast various pore environments with appropriate deconvolutions as shown in dotted lines in Figs. 4(c) and 4(d), respectively (the ratios of Q2:Q3:Q4 are 1:14:15 for sc-h-GFC.1 h and 1:20:25 for sc-GFC.3 h). The Q2 and Q3 environments observed in the sc-h-GFC.3 h thus decrease from those observed in the sc-h-GFC.1 h. Regarding the 1H MAS NMR spectra, signals observed in spectra of sc-h-GFC.1 h and sc-h-GFC.3 h (Fig. 5) are assignable as follows; 1) the 7-ppm shoulder is assignable to adsorbed water;24) 2) the 4-ppm signal observed in the spectrum of sc-h-GFC.1 h is the hydrogen-bonded silanol groups;25) 3) the 0.5-ppm signal and the 1.8-ppm shoulder are assignable to isolated silanol groups.23) The difference in the positions of 4-ppm signal in the spectrum of sc-h-GFC.1 h and 3.8-ppm signal in the spectrum of sc-h-GFC.3 h is likely due to the degree of hydrogen bond.25) Based on the 1H signal integrals with appropriate deconvolutions as shown in dotted lines in Fig. 5, the silanol group contents of sc-h-GFC.1 h and sc-h-GFC.3 h are estimated at 48 and 30 mmol/g, respectively.

The present mechanism of the micropore formations is as follows. Based on the 29Si and 1H MAS NMR spectra, the ratios of Q2 and Q3 per Q4 [(Q2 + Q3)/Q4], elemental analyses, and 1 type-nitrogen adsorption/desorption isotherms, the silanol groups form in sc-h-GFC upon its alkaline leaching by HCl (aq.) to generate micropores in sc-h-GFC. This is well-consistent with the reported formation mechanisms of porous oxide glasses.27) After the micropore formation, the silanol groups are condensed to decrease the GFC porosity, a common feature of silica solgel chemistry, where the condensation reaction involving silanol groups occurs under acidic conditions, resulting in an increase in the Si–O–Si bands to decrease the product porosity.28) The present mechanism is, therefore, ordinary for both chemistries of glass and silica.27,28 Such mechanisms have also been proposed before ca. 40 year11) in GFC studies, although there was a lack of detailed characteristics. They are, however, clearly compensated with the present 29Si and 1H MAS NMR spectra of non-crack microporous GFCs, where the formation of crack-based pores and subsequent healing seems to hardly occur during the acid treatment. Additionally, the present microporous GFC without cracks can be treated similarly to that of amorphous silicas, which have showed vast various poros-
ities,28) support properties,29)–31) and functionalities via surface modifications.32)

5. Conclusions

We have successfully demonstrated the preparation of microporous GFC without cracking via the heat treatment and subsequent slow cooling and acid treatment of GFC; acid treatment times of both 1 and 3 h are effective under the relatively strong acid condition. Since microporous GFC has been used as both an adsorbent and a catalyst14) even if the microporous GFC possessed cracks, the support property of the present microporous GFCs are worth further investigating accompanied with the mechanical stability of the products with different acid treatment time. These directions are being done in our laboratory, and we will do our best to continue our study.

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