Synthesis of microporous amorphous silica from perhydropolysilazane chemically modified with alcohol derivatives

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Perhydropolysilazane (PHPS) was chemical modified with alcohol derivative (ROH, R = CH3, i-C3H7, n-C5H11, n-C10H21) at the silicon (Si) of PHPS/ROH molar ratio of 4/1. The alkoxy group-functionalized PHPS was converted into amorphous silica powders by curing at 270°C to promote oxidative crosslinking, followed by pyrolysis at 600°C in air to complete the polymer/amorphous silica conversion. Thermogravimetric analysis in air of the 270°C-crosslinked PHPS showed an approximately 18% weight gain at 200 to 500°C. This weight gain was suppressed consistently with the number of carbon atoms of the alkoxy groups introduced to PHPS. Upon heating to 600°C, the PHPS modified with n-C10H21OH showed a total weight loss of 12%, and further weight loss of 31% was observed for the PHPS modified with n-C10H21OH. The nitrogen sorption analysis revealed that micropore volume of the polymer-derived amorphous silica increased consistently with the weight loss during the pyrolysis up to 600°C, and the amorphous silica derived from the PHPS modified with n-C10H21OH exhibited the highest micropore volume. Further increase in the micropore volume was achieved by increasing the Si/n-C10H21OH molar ratio from 4/1 to 2/1. The micropore volume and specific surface area of the resulting amorphous silica powders were 0.193 cm3/g and 370 m2/g, respectively.

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1. Introduction

The advancement of ceramic processing in the last few decades has resulted in various types of ceramic materials being synthesized and characterized for wide range application. The organometallic precursor route is one of the ceramic processing methods that received considerable attention since it offers several advantages as compared to conventional powder processing methods such as purity control, compositional homogeneity in the ceramic end-product and lower processing temperatures in ceramic preparation.1-3 In addition, this route offers opportunities to synthesize advanced silicon-based non-oxide ceramics such as silicon nitride (Si3N4)-based ceramics, and there have been several reports on the synthesis of Si3N4-based ceramics from polysilazanes.4,5 Especially, perhydropolysilazane (PHPS) has some advantages in high purity and high ceramic yield.6 Furthermore, PHPS contains many reactive Si-H and N-H groups which can react with chemical modifiers to yield novel ternary or quaternary Si-based non-oxide ceramics.7-10 In addition, PHPS has also received considerable attention as a favorable precursor for synthesizing pure silica because PHPS can be easily oxidized to yield pure silica with high ceramic yield.11 Recently, Iwamoto et al.12 has reported an approach in controlling the micro- and meso-porous structure formation by using organo-substituted polysilazane precursor. The organo-substituted group acted as a “sacrificial template” during polymer to ceramic conversion by heat treatment in air, which leading to the micro- and meso-porous structure formation. Owing to this feature, PHPS to silica conversion has a potential to be used in the fabrication of microporous amorphous silica-based membranes for gas separation.12,13 In this study, as sacrificial templates for microporous structure formation, alkoxy groups were introduced to PHPS by using an alcohol derivative as a chemical modifier, and converted the polymer into amorphous silica by heat treatment in air. The chemical modification reaction of PHPS with various alcohol derivatives was studied using 1H-NMR and FT-IR spectroscopic analyses. Then, the polymer/ceramic conversion behaviors, and the relationships between the chemical structure of alkoxy groups, thermal properties of the chemically modified PHPSs and the microporous structure formation were studied and discussed from a viewpoint to develop a novel method for synthesizing microporous amorphous silica-based materials through polymer precursor route.

2. Experimental procedures

2.1 Precursor synthesis

Commercially available perhydropolysilazanes (PHPS, Type NN110, 20% xylene solution, AZ Electronic Materials, Japan) was used as a starting polymer. In this study, alcohol derivatives of methanol (CH3OH), i-propanol [CH(CH3)2OH], n-pentanol (n-C5H11OH) and n-decanol (n-C10H21OH) were used for the chemical modification of PHPS. The reaction between as-
received PHPS and the alcohol derivative was carried out under dry argon (Ar) atmosphere using Schlenk techniques.\textsuperscript{15} The molar ratio of the reactants was set at the Si of PHPS/ROH molar ratio of 4/1. Then, the molar ratios of 8/1 and 2/1 were further investigated for the PHPS chemically modified with n-C\textsubscript{10}H\textsubscript{21}OH.

To the xylene solution of as-received PHPS, the alcohol derivative was added dropwise under magnetic stirring at room temperature. After the addition was completed, the mixture was refluxed for 1 h under flowing Ar. After cooling down to room temperature, the xylene was removed from the reaction mixture under vacuum to give an alcohol adduct as viscous liquid.

### 2.2 Oxidative crosslinking and Pyrolysis

To control the vigorous oxidation reaction in air, the thermal conversion process in this study was divided into the following two steps; 1) Polymer precursor was cured by heating at 270°C in air to promote oxidative crosslinking with a heating rate of 100°C/h and dwell time of 1 h in an alumina tube furnace. After cooling down to room temperature, the crosslinked polymer was obtained as white solid. 2) The crosslinked polymer precursor was ground to a fine powder using a mortar and pestle, then pyrolyzed in a furnace under flowing air by heating from room temperature to 600°C in 6 h, maintaining the temperature at 600°C for an additional 1 h, and finally cooling down to room temperature to give amorphous silica as white powders.

### 2.3 Characterization

Fourier transform infrared (FT-IR) spectra of the polymers, crosslinked and pyrolyzed products were recorded on KBr pellets in the wavenumber range of 4000–400 cm\textsuperscript{-1} (Model FT-IR/4200 IF, Jasco, Japan).\textsuperscript{1,14} \textsuperscript{1}H nuclear magnetic resonance (NMR) spectra were recorded for the polymers in CDCl\textsubscript{3} solution at room temperature (Model AV-400N, Bruker, USA). Thermogravimetric analysis (TGA) was performed on the crosslinked precursors up to 1000°C at a heating rate of 100°C/h under air (Model TG8120, Rigaku, Tokyo, Japan).

The pore size distribution of the pyrolyzed samples was measured using nitrogen (N\textsubscript{2}) sorption technique with the relative pressure of the N\textsubscript{2} gas ranging from 0 to 0.99 (Model Belsorp IF, Jasco, Japan).\textsuperscript{15} \textsuperscript{1}H nuclear magnetic resonance (NMR) spectra of the polymers, crosslinked and pyrolyzed products were recorded on KBr pellets in the wavenumber range of 4000–400 cm\textsuperscript{-1} (Model FT-IR/4200 IF, Jasco, Japan).\textsuperscript{1,14} \textsuperscript{1}H nuclear magnetic resonance (NMR) spectra were recorded for the polymers in CDCl\textsubscript{3} solution at room temperature (Model AV-400N, Bruker, USA). Thermogravimetric analysis (TGA) was performed on the crosslinked precursors up to 1000°C at a heating rate of 100°C/h under air (Model TG8120, Rigaku, Tokyo, Japan).

The pore size distribution of the pyrolyzed samples was measured using nitrogen (N\textsubscript{2}) sorption technique with the relative pressure of the N\textsubscript{2} gas ranging from 0 to 0.99 (Model Belsorp Max, BEL Japan Inc., Osaka, Japan). The micropores ($r_{pore} < 2.0$ nm) and mesopores (2.0 nm $\leq r_{pore} < 50$ nm) of the polymer-derived amorphous silica were characterized by the SF\textsuperscript{15} and BJH\textsuperscript{16} method, respectively.

### 3. Results and discussion

#### 3.1 Chemical structure of precursors

The chemical structure of the polymer precursors were studied by the FT-IR spectroscopic analysis. As shown in Fig. 1(a), as-received PHPS exhibits absorption bands at 3400 cm\textsuperscript{-1} (\nu(N–H)), 1180 cm\textsuperscript{-1} (\delta(N–H)) and 840–1020 cm\textsuperscript{-1} (\delta(Si–N–Si)).\textsuperscript{15,16} The spectra of PHPS modified with CH\textsubscript{3}OH [Fig. 1(b)] and that with i-C\textsubscript{3}H\textsubcript{7}OH [Fig. 1(c)] present additional absorption bands at 2950–2850 cm\textsuperscript{-1} (\nu(C–H)), 1450 cm\textsuperscript{-1} (\delta(CH\textsubscript{3})), and 1090 cm\textsuperscript{-1} (\nu(Si–OR)).\textsuperscript{15} However, the intensity of the absorption bands due to the C–H bond in the spectrum of PHPS modified with i-C\textsubscript{3}H\textsubscript{7}OH is relatively weak, suggesting that the reactivity of i-C\textsubscript{3}H\textsubscript{7}OH to PHPS was not sufficient due to the steric hindrance caused by the bulky secondary alkyl group. On the other hand, in the spectra of PHPS modified with n-C\textsubscript{10}H\textsubscript{21}OH [Fig. 1(d)] and that with n-C\textsubscript{10}H\textsubscript{21}OH (Fig. 1(e)), the intensity of the absorption bands due to the C–H bond remarkably increased.

The reaction between PHPS and alcohol derivative was further studied by \textsuperscript{1}H-NMR spectroscopic analysis. As a typical result, the \textsuperscript{1}H-NMR spectrum of PHPS chemically modified with n-C\textsubscript{10}H\textsubscript{21}OH is shown and compared with those of starting compounds, as-received PHPS and n-C\textsubscript{10}H\textsubscript{21}OH in Fig. 2(a). The peak assignment for the n-C\textsubscript{10}H\textsubscript{21}OH is also shown in this figure.\textsuperscript{15} As-received PHPS presents broad peaks at 5.2–4.5, 4.3 and 1.8–1.0 ppm assigned to SiH\textsubscript{2}/SiH\textsubscript{3}, SiH\textsubscript{3} and NH, respectively.\textsuperscript{15,16} The \textsuperscript{1}H-NMR spectrum of the PHPS chemically modified with n-C\textsubscript{10}H\textsubscript{21}OH mainly consists of the peaks of PHPS and the C\textsubscript{10}H\textsubscript{21} group. However, the peak of an alcoholic proton (H\textsubscript{2}) at 1.5 ppm disappears and the peaks of the n-C\textsubscript{10}H\textsubscript{21} group are broader in comparison with those in the spectrum of the starting n-C\textsubscript{10}H\textsubscript{21}OH, indicating the influence of the polymer network of PHPS. As shown in Fig. 2(b), with increasing the Si/n-C\textsubscript{10}H\textsubscript{21}OH molar ratio from 8/1 to 2/1, the intensity of the broad peak centered at 4.74 ppm within the peaks due to SiH\textsubscript{2}/SiH\textsubscript{3} decreased, and at the Si/n-C\textsubscript{10}H\textsubscript{21}OH molar ratio = 2/1, a new signal at 4.69 ppm begins to appear as a small shoulder.

![Fig. 1. IR spectra of polymer state and thermally treated in air of (a) PHPS, (b) PHPS modified with CH\textsubscript{3}OH, (c) PHPS modified with CH(CH\textsubscript{3})\textsubscript{2}OH, (d) PHPS modified with C\textsubscript{5}H\textsubscript{11}OH and (e) PHPS modified with n-C\textsubscript{10}H\textsubscript{21}OH (* indicating background, absorption due to CO\textsubscript{2}g).](image-url)
on the peak of HSiN\(_2\)/H\(_2\)SiN\(_2\) (marked by an arrow), which indicating the formation of HSiON\(_2\) groups\(^9\)

These FT-IR and \(^1\)H-NMR spectroscopic data indicate that the alcohol derivative mainly reacted with H\(_2\)SiN\(_2\) groups of PHPS to form RO–SiH\(_2\)N\(_2\) groups\(^9\).

### 3.2 Cross-linked polymers and their conversion into amorphous silica powders

The 270°C-crosslinked PHPS exhibits a new absorption band at 3400 cm\(^{-1}\) (SiOH),\(^10\) and decreases in intensity of the absorption bands due to the Si–H (2150 cm\(^{-1}\)), N–H (1180 cm\(^{-1}\)) and Si–N–Si (840–1020 cm\(^{-1}\)). After pyrolysis at 600°C in air, the absorption bands derived from PHPS completely disappeared and the Si–O absorption band intensity increased, indicating that PHPS was fully oxidized and converted into amorphous silica [Fig. 1(a)]. In the spectra of the 270°C-crosslinked samples derived from chemically modified PHPSs, the C–H absorption bands were still detected as minor peaks, then completely disappeared after the pyrolysis at 600°C in air. Thus, all the crosslinked samples were successfully converted into amorphous silica [Figs. 1(b)–1(e)].

To study the crosslinked polymer/amorphous silica conversion process in more detail, thermogravimetric (TG) analysis was performed. The results were summarized and shown in Fig. 3. The weight change of the crosslinked PHPS could not be clearly observed in the temperature range below 200°C. Then, a significant weight gain was observed as much as 13% at 200 to 500°C. Above 600°C, the sample weight slightly decreased, and the total weight gain measured at 1000°C was 12%.

The 270°C-crosslinked samples derived from PHPSs having alkoxy groups show a slight weight loss below 200°C, then the similar weight gain was for the samples derived from PHPS having CH\(_2\)OH groups and that having i-C\(_5\)H\(_{11}\)O groups. However, the weight gain at 200 to 500°C decreased consistently with the number of carbon atoms of the alkoxy groups introduced to PHPS. Upon heating to 600°C, the 270°C-crosslinked PHPS modified with n-C\(_{10}\)H\(_{21}\)OH showed a total weight loss of 12%, and the higher weight loss of 31% was observed for the sample derived from PHPS modified with n-C\(_{10}\)H\(_{21}\)OH (Fig. 3).

The weight gain observed for the crosslinked PHPS can be explained by the oxidation reactions like Eqs. (1) and (2), while one possible reason suggested for the slight weight loss above 600°C is the dehydration reaction shown in Eq. (3).

\[
\text{[SiH}_2\text{–NH}]_{n} + n\text{O}_2 \rightarrow n\text{SiO}_2 + n\text{NH}_3 \uparrow \quad (1)
\]
\[
2 \equiv\text{Si–H} + \text{O}_2 \rightarrow 2 \equiv\text{Si} – \text{OH} \quad (2)
\]
\[
2 \equiv\text{Si–OH} \rightarrow \equiv\text{Si–O} – \text{Si} \equiv + \text{H}_2\text{O} \quad (3)
\]

The weight loss below 200°C observed for the samples derived from chemically modified PHPSs was partly due to the evaporation of solvent remained. As shown in Fig. 4, the weight loss at 200 to 500°C increased consistently with the number of n-C\(_{10}\)H\(_{21}\)O groups by increasing the amount of n-C\(_{10}\)H\(_{21}\)OH in the chemical modification of PHPS, i.e., Si/n-C\(_{10}\)H\(_{21}\)OH molar ratio from 8/1 to 2/1. Thus, the significant weight loss observed for the samples derived from PHPS having n-C\(_{10}\)H\(_{21}\)OH groups and that having n-C\(_{10}\)H\(_{21}\)O groups was mainly attributed to the decomposition and elimination of the alkoxy groups.

### 3.3 Porous structure of polymer-derived amorphous silica powders

The textural properties of the polymer-derived amorphous silica were studied by the N\(_2\) physisorption at −196°C (77K),...
and the adsorption/desorption isotherms are shown in Fig. 5. The PHPS-derived amorphous silica presents a type III isotherm in the IUPAC classification, indicating non-porous. The similar type III isotherm was observed for the amorphous silica samples derived from PHPS having CH\textsubscript{3}O groups and that having i-C\textsubscript{3}H\textsubscript{7}O groups.

On the other hand, the isotherm of amorphous silica derived from PHPS having n-C\textsubscript{5}H\textsubscript{11}O groups presents a transitional type between typical type I and type IV without hysteresis loops. The N\textsubscript{2} uptake at the relative pressure lower than \(p/p_0 = 0.2\) reveals the micropore filling, while another slight uptake at \(p/p_0 = 0.85\) and above is thought to be due to the meso- and/or macroporosity generated by agglomeration of the powdered sample. Thus, the isotherm of this sample is ascribed to type I-related microporous material.

The isotherm of amorphous silica derived from PHPS having n-C\textsubscript{10}H\textsubscript{21}O groups also presents a similar transitional type, and the N\textsubscript{2} uptake below \(p/p_0 = 0.2\) is remarkably increased.

Figure 6(a) shows the pore size distribution (PSD) curves obtained for the polymer-derived amorphous silica. The PSD curves for the micropores (\(r_{\text{pore}} < 2.0\) nm) and those for mesopores (\(2.0\) nm \(\leq r_{\text{pore}} < 50\) nm) were characterized by the SF\textsuperscript{15}) and BJH\textsuperscript{16}) method, respectively. The micropore volume of these samples are plotted as a function of number of carbon atoms in the alkoxy groups and shown in Fig. 6(b). Compared with the three kinds of non-porous amorphous silica samples, an apparent enhancement in the micropore volume can be observed while longer organic chain of alkoxy groups were introduced to PHPS. The PSD curve of amorphous silica derived from PHPS having n-C\textsubscript{5}H\textsubscript{11}O groups was detected in the range of 0.43–0.84 nm and peaked at 0.5 nm with micropore volume about 0.038 cm\textsuperscript{3}/g. By introducing n-C\textsubscript{5}H\textsubscript{11}O groups, micropores having a size range of 0.43–1.3 nm were detected, and the PSD curve exhibited a peak top at 0.43 nm with the micropore volume about 0.173 cm\textsuperscript{3}/g. This micropore volume is highest among the five samples, and approximately four times higher than that derived from PHPS having n-C\textsubscript{5}H\textsubscript{11}O groups.

The effect of varying Si/ROH molar ratio in the PHPS chemical modification was further studied by using n-C\textsubscript{10}H\textsubscript{21}OH. The results are summarized and shown in Figs. 7 and 8. By varying the molar ratio, the PSD curves located in the range of 0.43–1.3 nm are quite similar, and the height of the peak top at 0.43 nm apparently increased when the molar ratio increased to 2/1. As shown in Fig. 8(b), the resulting micropore volume increased linearly with the molar ratio, and reached 0.193 cm\textsuperscript{3}/g at the molar ratio = 2/1.

However, both of the weight loss during the pyrolysis and the resulting micropore volume of the pyrolyzed sample were not
increased linearly with the amount of the n-C\textsubscript{10}H\textsubscript{21}OH used for the chemical modification of PHPS. This could be due to the formations of the oligomers or monomers. As previously reported, it during the chemical modification of PHPS with alcohol derivatives, Si-N bond cleavage of PHPS could be occurred to some extent, and the resulting by-products of the oligomers and/or monomers having the alkoxy groups were thought to be evaporated during the solvent removal under vacuum and/or oxidative crosslinking up to 270°C. The amount of the by-products was thought to be increased consistently with the amount of n-C\textsubscript{10}H\textsubscript{21}OH used for the chemical modification of PHPS, which leading to the decrease in the efficiency of the micropore formation.

On the other hand, the alkoxy groups introduced to the polymer network of PHPS completely decomposed during the pyrolysis up to 600°C (Fig. 1), and the microporous structure development was found to be observed for the samples which exhibited the apparent weight loss at 200–500°C during the pyrolysis (Figs. 3 and 4). Moreover, the micropore volume was found to be increased consistently with the weight loss, and especially, n-C\textsubscript{10}H\textsubscript{21}OH was found to be effective for the micropore formations. These results reveal that the thermal decomposition of the organic groups is essential for the microporous structure development of the polymer-derived amorphous silica investigated in this study.

The shape of the isotherms and the PSD curves characterized for the amorphous silica suggest some potential of the polymer route in this study as a novel method to synthesize supermicroporous amorphous silica-based materials for energy application such as a highly efficient catalyst support and a gas separation membrane.

4. Summary

In this study, commercially available PHPS was chemical modified with alcohol derivative (ROH, R = CH\textsubscript{3}, i-C\textsubscript{3}H\textsubscript{7}, n-C\textsubscript{5}H\textsubscript{11}, n-C\textsubscript{10}H\textsubscript{21}). The alkoxy group-functionalized PHPS was converted into amorphous silica powders by oxidative crosslinking at 270°C and subsequent pyrolysis at 600°C in air. The results can be summarized as follows:

1. FT-IR and \textsuperscript{1}H-NMR spectroscopic analyses revealed that the alcohol derivative mainly reacted with H\textsubscript{2}SiN\textsubscript{2} groups of PHPS to form RO-SiHN\textsubscript{2} groups.

2. As-received PHPS and the alkoxy group-functionalized PHPS were successfully converted into amorphous silica by the two-step heat treatment in air.

3. The results of pore size distribution analysis revealed that the microporosity of polymer-derived amorphous silica increased with the number of carbon atoms of ROH used as a chemical modifier for PHPS, and a significant increase in the micropore volume was observed for the amorphous silica when n-C\textsubscript{10}H\textsubscript{21}OH was used as the chemical modifier.

4. It was also found that the micropore volume could be enhanced with increasing the amount of n-C\textsubscript{10}H\textsubscript{21}OH used for the chemical modification, and reached 0.193 cm\textsuperscript{3}/g at the molar ratio = 2/1.

5. The micropore volume increased consistently with the weight loss detected at 200 to 500°C, and it was found to
be essential for the microporous structure development that the thermal decomposition of the alkoxy groups introduced to PHPS.

(6) The textural properties of the polymer-derived amorphous silica suggested some potential of this polymer route to develop a novel method for synthesizing super-microporous amorphous silica-based materials.

References
1) R. W. Rice, *Am. Ceram. Soc. Bull.*, 62, 889–892 (1983).
2) K. J. Wynne and R. W. Rice, *Annu. Rev. Mater. Sci.*, 14, 297–334 (1984).
3) R. Riedel and W. Dressler, *Ceram. Int.*, 22, 233–239 (1996).
4) D. Seyferth, C. Strohmann, N. R. Dando and A. Perrotta, *J. Chem. Mater.*, 7, 2058–2066 (1995).
5) E. Kroke, Y.-L. Li, C. Konetschny, E. Lecomte, C. Fasel and R. Riedel, *Mater. Sci. Eng., R*, 28, 97–199 (2000).
6) O. Funayama, M. Arui, Y. Tashiro, H. Aoki, T. Suzuki, K. Tamura, H. Kaya, H. Nishii and T. Isoda, *J. Ceram. Soc. Japan*, 98, 104–107 (1990).
7) O. Funayama, T. Kato, Y. Tashiro and T. Isoda, *J. Am. Ceram. Soc.*, 76, 717–723 (1993).
8) O. Funayama, Y. Tashiro, T. Aoki and T. Isoda, *J. Ceram. Soc. Japan*, 102, 908–912 (1994).
9) Y. Iwamoto, K. Kikuta and S. Hirano, *J. Mater. Res.*, 13, 353–361 (1998).
10) Y. Iwamoto, K. Kikuta and S. Hirano, *J. Ceram. Soc. Japan*, 108, 350–356 (2000).
11) T. Kubo and H. Kozuka, *J. Ceram. Soc. Japan*, 114, 517–523 (2006).
12) Y. Iwamoto, K. Sato, T. Kato, T. Inada and Y. Kubo, *J. Eur. Ceram. Soc.*, 25, 257–264 (2005).
13) Y. Iwamoto, *J. Ceram. Soc. Japan*, 115, 947–954 (2007).
14) D. F. Shiver and M. A. Drezdzon, “The manipulation of air sensitive compounds”, 2nd Edition, John Wiley & Sons, Inc. (1986) pp. 30–44.
15) A. Saito and H. C. Foley, *AIChE J.*, 37, 429–436 (1991).
16) P. Barrett, L. G. Joyner and P. H. Halenda, *J. Am. Chem. Soc.*, 73, 373–380 (1951).
17) D. Seyferth, G. Wiseman and C. Prud’homme, *J. Am. Ceram. Soc.*, 66, C-13–C-14 (1983).
18) R. M. Silverstein, G. C. Bassler and T. C. Morrill, “Spectroscopic Identification of Organic Compounds”, 5th Edition, John Wiley & Sons, Inc. (1991).