

Formation of Reactive Microporous Networks from Alkoxyvinylsilylated Siloxane Cages

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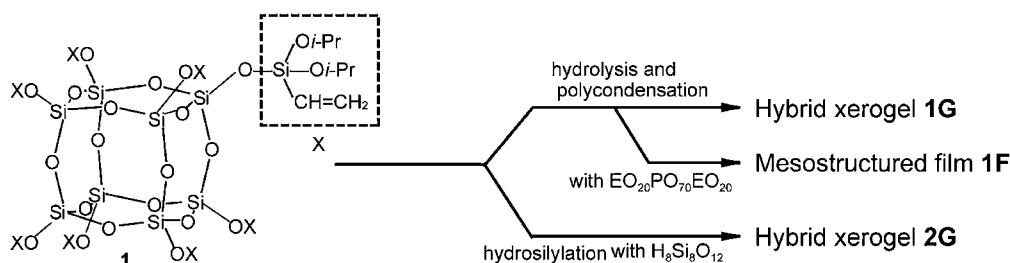
A bifunctional siloxane cage, where double four-membered ring (D4R) silicate was capped with alkoxyvinylsilyl groups, was synthesized as a novel building block for the formation of inorganic–organic microporous solids in order to show its usefulness for synthesizing silica-based nanomaterials with unique structures and properties. The nanobuilding blocks were connected to each other either by hydrolysis and condensation of alkoxyvinyl groups to form Si–O–Si linkages or by hydrosilylation of vinyl groups with hydrogen-terminated D4R ($\text{H}_8\text{Si}_8\text{O}_{12}$), which was used as a linking agent, to form Si–CH₂CH₂–Si linkages. Xerogel obtained by hydrosilylation showed a significant increase in the surface area upon removal of alkoxy groups by post treatment. The molecular design of bifunctionally-silylated D4R units provides a new approach to the formation of microporous networks with uniform distribution of reactive groups that allow post-modification.

Nanoporous silica-based materials are widely used as catalysts, adsorbents, and membranes.^{1–4} Among various synthetic routes to such materials, a building block approach based on the interconnection of well-defined siloxane species has received significant interest.⁵ The use of designed oligomeric precursors leads to a better control of the final structures and properties than that of conventional monomeric precursors, such as tetraalkoxysilanes and organotrialkoxysilanes.

The siloxane cage with a double four-membered ring (D4R) structure is particularly useful as a building block because of its rigid and symmetric framework.^{6–9} The D4R structure with specific Si–O–Si angles and very small internal space, being able to accommodate atomic hydrogen and fluoride ions,^{10–12} provides unique properties different from those derived from amorphous networks. Si atoms on the corners can partly be replaced with other elements like Al and Ti, which will also lead to the design of well-defined heterogeneous catalysts. D4R derivatives with the general formula of $\text{RSi}_8\text{O}_{12}$, where R = H or organic groups, can be obtained by hydrolysis and polycondensation of the corresponding trifunctional silanes.^{13–16} It

is also known that D4R silicate anions ($\text{Si}_8\text{O}_{20}^{8-}$) are formed almost quantitatively from various silicate sources in aqueous solutions of tetramethylammonium hydroxide,^{17–20} and can be functionalized at all corners by silylation with a variety of organochlorosilanes.^{21–28} The construction of porous solids by interconnecting these D4R-derivatives with Si–O–Si or Si–R–Si linkages have been extensively studied so far.^{29–43} We have recently reported the synthesis of silica-based nanomaterials from alkoxyvinylated D4R units ($\text{Si}_8\text{O}_{12}(\text{OSiMe}_{3-n}(\text{OEt})_n)_8$, $n = 1–3$).⁴⁴ These derivatives form siloxane networks by sol–gel processes, and the resulting xerogels exhibited different structures and surface areas, depending on the number of alkoxy groups (n). Therefore, it is quite interesting to design silicate-based D4R units in a more sophisticated way to prepare silica-based nanomaterials incorporating functional groups instead of methyl groups within the structures.

In this paper, we report the synthesis of two types of microporous solids by using bifunctional, alkoxyvinylsilylated D4R siloxane cage as a novel nanobuilding block (Scheme 1). The first one is prepared by hydrolysis and polycondensation of



Scheme 1. Formation of microporous networks from alkoxyvinylsilylated D4R silicate **1**.

alkoxy groups to form porous siloxane networks, while vinyl groups remain intact. The other is prepared by hydrosilylation of vinyl groups with various linkers, containing $\equiv\text{SiH}$ groups, to form ethylene-bridged siloxane networks while alkoxy groups largely remain. Because there are lots of substances possessing $\equiv\text{SiH}$ groups, novel hybrid materials can be designed by appropriate selection of starting materials. In this study we have chosen hydrogen-terminated D4R ($\text{H}_8\text{Si}_8\text{O}_{12}$) because it also acts as a building block. In both of the systems, functional groups, i.e., vinyl groups or alkoxy groups, can be uniformly placed in the porous networks, which provides a unique opportunity for post modification.

Experimental

Materials. Cage-like octameric tetramethylammonium (TMA) silicate ($\text{TMA}_8\text{Si}_8\text{O}_{20}\cdot x\text{H}_2\text{O}$) with a double four-membered siloxane ring was prepared by hydrolysis and polycondensation of tetraethoxysilane (Tokyo Kasei Kogyo) in an aqueous solution containing tetramethylammonium hydroxide pentahydrate ($(\text{CH}_3)_4\text{N}(\text{OH})\cdot 5\text{H}_2\text{O}$, Sigma-Aldrich, 97%). Hydrated crystals obtained by concentrating the resulting solution were vacuum dried to reduce the water content (where x was decreased from 65 up to 29).⁴⁴ Trichlorovinylsilane (Tokyo Kasei Kogyo, >98%) and 2-propanol (dehydrated, Wako Pure Chemical Industries, 99.5%) were used for the synthesis of silylating agent of chlorodiisopropoxyvinylsilane ($\text{Vi}(i\text{-PrO})_2\text{SiCl}$). $\text{H}_8\text{Si}_8\text{O}_{12}$ was synthesized from trichlorosilane (Tokyo Kasei Kogyo, >98%) according to a literature procedure.⁴⁵ Poly(oxyethylene)-poly(oxypropylene)-poly(oxyethylene)-type triblock copolymer ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, P123) was purchased from Sigma-Aldrich and used for the synthesis of mesostructured films. Platinum tetramethyldivinylsiloxane complex in xylene (2 wt %) was obtained from Sigma-Aldrich and used as a catalyst for hydrosilylation. Other chemicals, including hexane (Kanto Chemical, 96%), pyridine, tetrahydrofuran (THF), toluene (dehydrated, Wako Pure Chemical Industries, 99.5%), KOH, 1 and 6 M HCl aq. (Wako Pure Chemical Industries) were used as received.

Synthesis of Chlorodiisopropoxyvinylsilane as Silylating Agent. The silylating agent was synthesized by the dropwise addition of 2-propanol (23.6 mL) into a mixture of trichlorovinylsilane (ViSiCl_3 , 25 g) and THF (50 mL) under nitrogen atmosphere. The molar ratio of 2-propanol to trichlorovinylsilane was 2. HCl gas generated by this reaction was passed out of the vessel and trapped by KOH aq. After the addition, the solvent, unreacted trichlorovinylsilane, and dichloroisopropoxyvinylsilane ($\text{Vi}(i\text{-PrO})\text{SiCl}_2$) were removed by stirring the mixture at 40 °C for 30 min under reduced pressure. The resulting clear liquid mainly consisting of chlorodiisopropoxyvinylsilane ($\text{Vi}(i\text{-PrO})_2\text{SiCl}$) (ca. 80%) and triisopropoxyvinylsilane ($\text{Vi}(i\text{-PrO})_3\text{Si}$) (ca. 20%) was used as the silylating agent without further purification. ^{29}Si NMR (99.3 MHz, CDCl_3): δ -46.6 ($\text{Vi}(i\text{-PrO})_2\text{SiCl}$), -62.3 ($\text{Vi}(i\text{-PrO})_3\text{Si}$). ^{13}C NMR (125.65 MHz, CDCl_3): δ 136.2 ($\text{SiCH}=\text{CH}_2$), 131.7 ($\text{SiCH}=\text{CH}_2$), 65.4 ($\text{SiOCH}(\text{CH}_3)_2$), 25.4 ($\text{SiOCH}(\text{CH}_3)_2$).

Synthesis of Alkoxyvinylsilylated D4R Silicate 1. Alkoxyvinylsilylated D4R silicate **1** was synthesized by silylation of D4R silicate ($\text{Si}_8\text{O}_{20}^{8-}$) with chlorodiisopropoxyvinylsilane ($\text{Vi}(i\text{-PrO})_2\text{SiCl}$). $\text{TMA}_8\text{Si}_8\text{O}_{20}\cdot 29\text{H}_2\text{O}$ crystal (2 g) dispersed in THF (20 mL) was added into a mixture of the silylating agent, pyridine (14.5 mL), and THF (100 mL) with vigorous stirring at 0 °C. The molar ratio of D4R/ $\text{Vi}(i\text{-PrO})_2\text{SiCl}$ /pyridine was

1/100/150. After stirring for 30 min, precipitates of pyridine hydrochloride were removed by filtration to give a clear solution. The precursor **1** ($(\text{Vi}(i\text{-PrO})_2\text{Si})_8\text{Si}_8\text{O}_{20}$) was isolated as a clear viscous liquid by the removal of the unreacted silylating agent, followed by gel permeation chromatography (GPC) using THF as the eluent.

Synthesis of Sol-Gel-Derived Hybrid Xerogel 1G. Hydrolysis and polycondensation of the precursor **1** was conducted in a mixture of THF, H_2O , and 6 M HCl. The molar ratio of **1**/THF/ H_2O /HCl was 1:16:16:0.64. The mixture was initially in an emulsion state, but it became a clear solution during stirring at room temperature and finally formed a transparent gel after 1 h. The xerogel **1G** obtained by drying under vacuum was pulverized before characterization.

Synthesis of Ethylene-Bridged Hybrid Gel 2G by Hydrosilylation with $\text{H}_8\text{Si}_8\text{O}_{12}$. Hydrosilylation of the precursor **1** with $\text{H}_8\text{Si}_8\text{O}_{12}$ was conducted in a mixture of platinum tetramethyldivinylsiloxane complex and toluene (20 mL per gram of **1**). The molar ratio of **1**/ $\text{H}_8\text{Si}_8\text{O}_{12}$ /Pt was 1:1:0.04. The mixture was stirred at room temperature for 3 h and then at 80 °C for 2 days in a closed vessel until gelation occurred. The hybrid gel **2G** obtained by washing with hexane and drying under vacuum was pulverized before characterization.

Characterization. Liquid-state ^{29}Si and ^{13}C NMR spectra were obtained on a JEOL Lambda-500 spectrometer with resonance frequencies of 99.25 and 125.65 MHz, respectively. Solid-state ^{29}Si and magic-angle spinning (MAS) NMR measurements were performed on a JEOL JNM-CMX-400 spectrometer at a resonance frequency of 79.42 MHz, with a pulse width of 45°, and a recycle delay of 100 s. Solid-state ^{13}C MAS NMR spectra were obtained on the same spectrometer at a resonance frequency of 100.54 MHz with a contact time of 5 ms and a recycle delay of 20 s. Deconvolution of the spectrum was performed by using a Gaussian function on Spinsight software ver. 4.3.2. Chemical shifts for ^{13}C and ^{29}Si NMR were referenced to tetramethylsilane at 0 ppm. Mass spectrometric results were acquired using a GC-Mate II by fast atom bombardment ionization. Powder X-ray diffraction (XRD) patterns were recorded on a Mac Science M03XHF22 diffractometer with Mn-filtered $\text{FeK}\alpha$ radiation or on a Rigaku RINT-Ultima III powder diffractometer with monochromated $\text{CuK}\alpha$ radiation. FT-IR spectra of the products in KBr pellets were obtained under vacuum using a JASCO FT/IR-6100 spectrometer with a nominal resolution of 0.5 cm^{-1} . Nitrogen adsorption-desorption measurements were performed with an Autosorb-1 instrument (Quantachrome Instruments, Inc.) at 77 K. Samples were preheated at 120 °C for 3 h under 1×10^{-2} Torr. BET surface areas were calculated from the data in the relative pressure range between 0.05 and 0.30. Water vapor adsorption isotherms at 25 °C were collected on a Belsorp 18 (Bel Japan, Inc.). Samples were outgassed at 120 °C for 8 h prior to the measurements.

Results and Discussion

Alkoxyvinylsilylation of D4R Silicate ($\text{Si}_8\text{O}_{20}^{8-}$). Figure 1a shows the ^{29}Si NMR spectrum of the precursor **1** (in CDCl_3) obtained by silylation of D4R silicate with chlorodiisopropoxyvinylsilane ($\text{Vi}(i\text{-PrO})_2\text{SiCl}$). The spectrum shows two signals at -69.1 and -110.7 ppm with the integral intensity ratio of 1:1. These signals can be assigned to the T^1 and Q^4 units of the silylated D4R silicate,⁴⁶ being shifted upfield from the T^0 signal of the silylating agent ($\text{Vi}(i\text{-PrO})_2\text{SiCl}$,

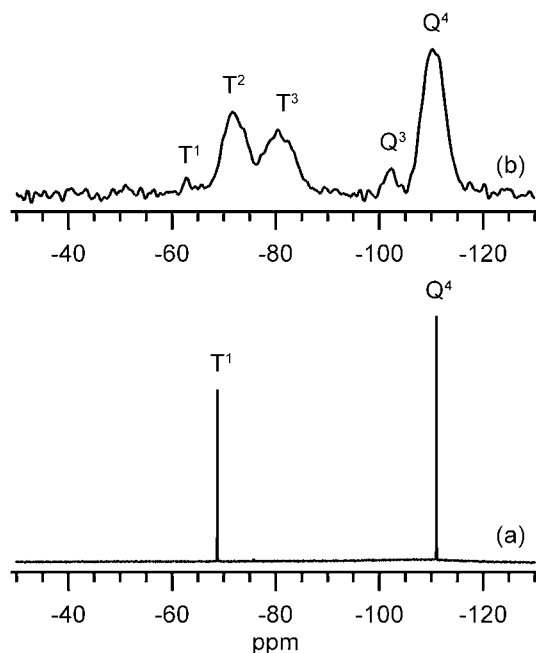


Figure 1. (a) Liquid-state ^{29}Si NMR spectrum of **1** in CDCl_3 and (b) solid-state ^{29}Si MAS NMR spectrum of **1G**.

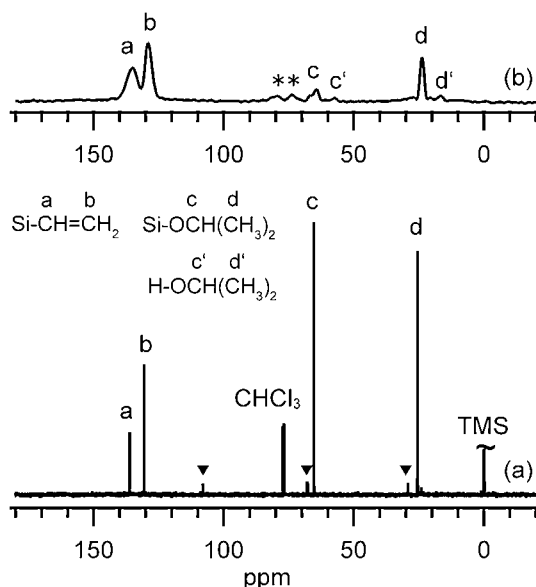


Figure 2. (a) Liquid-state ^{13}C NMR spectrum of **1** in CDCl_3 and (b) solid-state ^{13}C CP/MAS NMR spectrum of **1G** (*: SSB, $\blacktriangledown$: THF hydroperoxide).

–46.6 ppm) and the Q^3 signal of the D4R silicate ($(\text{Me}_4\text{N})_8\text{-Si}_8\text{O}_{20}\cdot 29\text{H}_2\text{O}$, –96.3 ppm), respectively. The ^{13}C NMR spectrum of **1** (Figure 2a) shows the signals of the vinyl group (136.1 ppm ($\text{SiCH}=\text{CH}_2$) and 130.5 ppm ($\text{SiCH}=\text{CH}_2$)) and the isopropoxy group (65.4 ppm ($\text{SiOCH}(\text{CH}_3)_2$) and 25.4 ppm ($\text{SiOCH}(\text{CH}_3)_2$)).⁴⁷ These results and the MS data (m/z found: 1930.1 $[\text{M} - \text{H}]^+$; calcd for $\text{C}_{64}\text{H}_{135}\text{O}_{36}\text{Si}_{16}$: 1929.5) indicate that all the corner Q^3 sites of D4R silicate were reacted with Si–Cl groups of the silylating agents with the retention of the vinyl and isopropoxy groups in the silylated product. Si–Cl groups in the silylating agent are more active for the reaction with Si–OH

(or Si–O[–]) corners than isopropoxy groups.⁴⁸ The precursor **1** was soluble in THF but not in ethanol, in contrast to diethoxy(methyl)silylated D4R⁴⁴ which is soluble both in ethanol and THF. This difference should be due to the decrease in the polarity of vinyl and isopropoxy groups if compared with methyl and ethoxy groups.

Vinyl groups of precursor **1** were not polymerized by thermal treatment with stirring in the presence of azobisisobutyronitrile, suggesting that the reactivity of the vinyl groups is suppressed by the presence of neighboring bulky isopropoxy groups. Because isopropoxy groups of **1** can be hydrolyzed, as shown later, the interactions between hydrolyzed silanol groups and poly(ethylene oxide) chains of triblock copolymer P123 ($(\text{EO})_{70}(\text{PO})_{20}(\text{EO})_{70}$) lead to the formation of a mesostructured film **1F** similar to that reported previously (Supporting Information, Figure S1).⁴⁴

Characterization of Sol–Gel-Derived Hybrid Xerogel **1G**.

The solid-state ^{29}Si MAS NMR spectrum (Figure 1b) of the xerogel **1G**, prepared by hydrolysis and polycondensation of **1**, shows five signals corresponding to T^m ($\text{ViSi}(\text{OH})_{3-m}(\text{OSi})_m$, $m = 1, 2$, and 3) and the Q^n ($\text{Si}(\text{OSi})_n(\text{OH})_{4-n}$, $n = 3$ and 4) units. From the $(\text{T}^2 + \text{T}^3)/(\text{T}^1 + \text{T}^2 + \text{T}^3)$ ratio, it is estimated that 94% of the terminal silyl groups of **1** are connected to each other via siloxane bonds. Also the $(\text{T}^2 + 2\text{T}^3)/2(\text{T}^1 + \text{T}^2 + \text{T}^3)$ ratio, which evaluates the degree of polymerization, suggests that 67% of isopropoxy groups formed siloxane bonds. These results indicate that eleven isopropoxy groups out of sixteen per precursor were polymerized at least. These values are comparable to those for the xerogel derived from $(\text{Me}(\text{EtO})_2\text{-Si})_8\text{Si}_8\text{O}_{20}$,⁴⁴ suggesting that both products have similar network structures. The presence of the Q^3 signal is indicative of the partial cleavage of the Si–O–Si bonds in **1**. However, the $\text{Q}^3/(\text{Q}^3 + \text{Q}^4)$ ratio (ca. 10%) is much smaller than that for the conventional silica xerogels prepared under similar conditions. The solid-state ^{13}C CP/MAS NMR spectrum (Figure 2b) shows the signals due to vinyl groups (ca. 130 ppm) together with small signals of the residual isopropoxy groups. The relative signal intensity ratio of isopropoxy to vinyl groups is much smaller than that for the precursor **1** (Figure 2a).

Figure 3 compares the FT-IR spectra of **1** and **1G**. The spectrum of **1** (Figure 3a) shows the presence of vinyl groups, as confirmed by the bands assigned to the C=C stretching vibration (1601 cm^{-1}) and the C–H stretching vibrations of $-\text{CH}=-$ (3022 cm^{-1}) and $=\text{CH}_2$ (3062 cm^{-1}). These bands are still observed for **1G** (Figure 3b), while the C–H stretching vibrations of $-\text{CH}_3$ (at 2975 and 2898 cm^{-1}) are significantly decreased by hydrolysis of isopropoxy groups. Both spectra also show the bands due to Si–O–Si network at 1000 – 1100 cm^{-1} and at around 550 cm^{-1} . Importantly, the band at 573 cm^{-1} , which is associated with the skeletal vibration of the double four-membered siloxane ring, is clearly observed for **1G**, suggesting that the D4R units are retained even after the reaction.^{38,43,49,50} The retention of the D4R units was also confirmed by the XRD pattern of **1G** (Supporting Information, Figure S2) to observe a broad peak at around $2\theta = 7^\circ$, being very similar to that of xerogel derived from diethoxy(methyl)silylated-D4R unit,⁴⁴ suggesting that a certain structural order is present. Also, the shoulder peak at 3643 cm^{-1} is indicative of the presence of silanol groups in the networks.¹

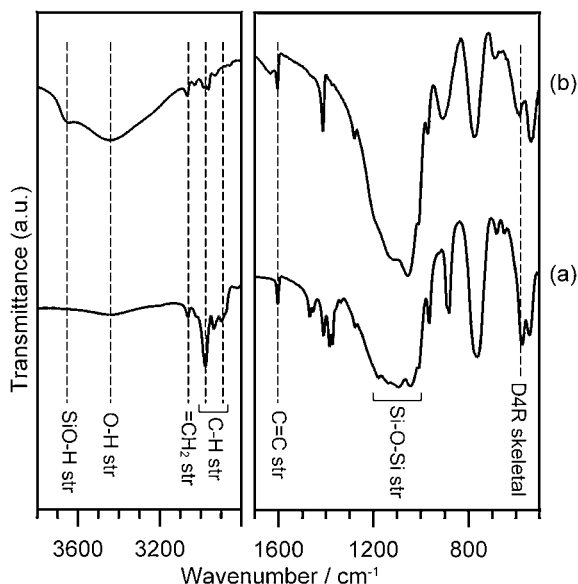


Figure 3. FT-IR spectra of (a) **1** and (b) **1G**.

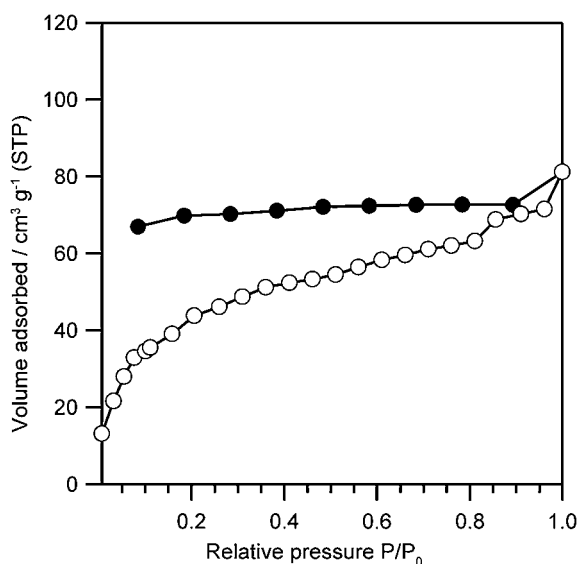


Figure 4. Nitrogen adsorption-desorption isotherms of **1G**. The open and filled symbols denote adsorption and desorption, respectively.

The nitrogen adsorption isotherm of **1G** (Figure 4) is basically classified into type I, characteristic of microporous silica, and the BET surface area is calculated to be $160 \text{ m}^2 \text{ g}^{-1}$. The isotherm shows a hysteresis not closed in the low relative pressure range. A similar isotherm has been reported by Morrison et al. for xerogel consisting of D4R units interconnected to each other via $\text{Si}-\text{CH}_2\text{CH}_2-\text{SiMe}_2-\text{CH}_2\text{CH}_2-\text{Si}$ linkages.³⁷ Such behavior may be attributed to the micropores with narrow windows with almost the same width of pore entrance as that of adsorbate molecules.⁵¹ In such cases, adsorption isotherms may not reflect stable equilibrium in adsorption measurements, and the flexibility of the networks may also affect the behavior. The decrease in the nitrogen uptake was observed when the same sample was measured again after the first measurement, which suggests irreversible deformation of

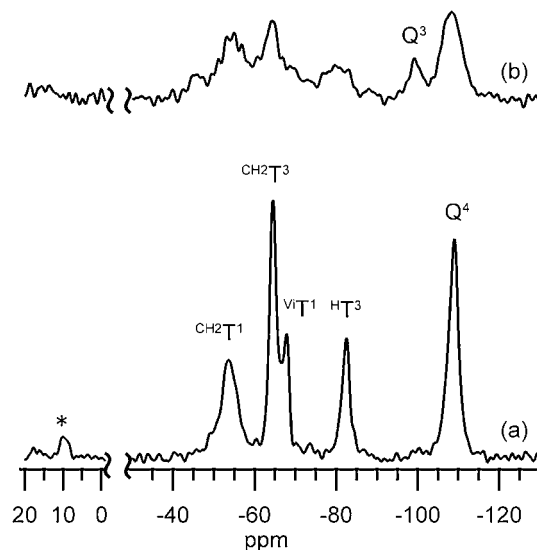


Figure 5. ^{29}Si MAS NMR spectra of ethylene-bridged hybrid xerogel **2G** (a) before and (b) after the acid treatment (*: Si due to tetramethyldivinyldisiloxane of the Pt catalyst).

the framework mainly due to the flexible Si–O–Si linkages. In contrast, the isotherm of xerogel derived from $(\text{Me}(\text{EtO})_2\text{Si})_8\text{Si}_8\text{O}_{20}$ (BET surface area is $600 \text{ m}^2 \text{ g}^{-1}$)⁴⁴ does not show such a hysteresis though both gels formed similar networks as described above. These results suggest that the accessible pores of **1G** become narrower probably due to the difference in size between methyl and vinyl groups inside pores.

Calcination of **1G** at 550°C greatly reduces the porosity (surface areas lower than $10 \text{ m}^2 \text{ g}^{-1}$) because of the serious structural deformation. The decrease in the IR absorption band due to D4R units (Supporting Information, Figure S3a) partly supports the deformation. The acid-treatment of **1G** with a mixture of HCl and EtOH also showed a similar decrease though the IR peak due to D4R units is observed for the acid-treated sample (Supporting Information, Figure S3b). The reason for this result is not well understood, but further condensation between remaining silanol groups in the networks could reduce the size of pore entrances of the sample.

Characterization of Ethylene-Bridged Hybrid Xerogel 2G. Figure 5a shows the ^{29}Si MAS NMR spectrum of **2G**. The signals at -53.8 and -64.5 ppm can be assigned to the ethylene-bridged T^1 and T^3 sites ($(\equiv\text{SiO})(i\text{-PrO})_2\text{Si}-\text{CH}_2\text{CH}_2-\text{Si}(\text{OSi})_3$), denoted as CH_2T^1 and CH_2T^3 , respectively) formed by hydrosilylation of the vinyl groups of **1** with SiH groups of $\text{H}_8\text{Si}_8\text{O}_{12}$.³⁶ The signals at -67.6 and -82.4 ppm are assigned to unreacted diisopropoxyvinylsilyl groups (denoted as ViT^1 site) of **1** and hydridosilyl groups (denoted as HT^3 site) of $\text{H}_8\text{Si}_8\text{O}_{12}$, respectively.³⁶ The integral intensity ratios of $\text{CH}_2\text{T}^1 / (\text{CH}_2\text{T}^1 + \text{ViT}^1)$ and $\text{CH}_2\text{T}^3 / (\text{CH}_2\text{T}^3 + \text{HT}^3)$ respectively, both indicating the degree of forming Si– CH_2CH_2 –Si linkages, are about 69% and 77%. Notably, in contrast to **1G**, the absence of Q^3 site in **2G** suggests that D4R units are mostly retained without the cleavage of Si–O–Si linkages. The residual Pt catalyst in **2G** is also confirmed by the presence of tetramethyldivinyldisiloxane, the signal of which appeared at

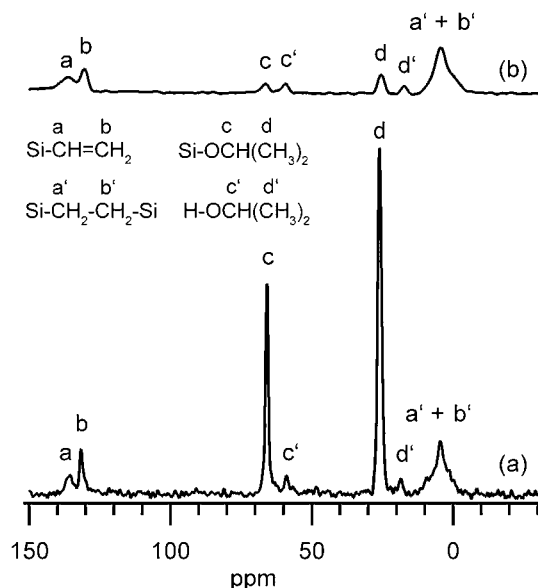


Figure 6. ^{13}C CP/MAS NMR spectra of ethylene-bridged hybrid xerogel **2G** (a) before and (b) after the acid treatment.

9.1 ppm. The ^{13}C CP/MAS NMR spectrum of **2G** (Figure 6a) shows a new signal at around 5 ppm assigned to ethylene groups, indicating the formation of $\text{Si}-\text{CH}_2\text{CH}_2-\text{Si}$ linkages. The signals due to isopropoxy groups (at 65.8 and 26.0 ppm) and unreacted vinyl groups (at 135.4 and 131.6 ppm) are also observed, respectively, which is consistent with the ^{29}Si MAS NMR data.

To examine the reactivity of alkoxy groups in the network of **2G**, the sample was acid-treated. By stirring it in a 1:1 mixture of EtOH and 1 M HCl, most of the isopropoxy groups are hydrolyzed and eliminated. After the acid treatment, the relative intensity ratios of the ^{13}C CP/MAS NMR signals of isopropoxy groups to those of ethylene bridges and residual vinyl groups in **2G** are significantly decreased (Figure 6b). However, the partial cleavage of the $\text{Si}-\text{O}-\text{Si}$ networks upon the acid treatment was revealed by ^{29}Si MAS NMR (Figure 5b). The $Q^3/(Q^3 + Q^4)$ ratio indicates that the degree of the cleavage is at least about 20%. All of the signals became broader after the acid treatment, which is possibly due to the variation in their environments caused by the cleavage and/or by the distortion of the siloxane networks by hydrolysis of the alkoxy groups.

The pore accessibility of **2G** before and after the acid treatment was investigated by nitrogen and water adsorption measurements. On the basis of the nitrogen adsorption/desorption isotherm of **2G** (Figure 7a), the BET surface area is calculated to be $80\text{ m}^2\text{ g}^{-1}$. When **2G** was calcined at 550°C , the BET surface area increased to $300\text{ m}^2\text{ g}^{-1}$ (data not shown). More strikingly, after the acid treatment the BET surface area noticeably increased up to $600\text{ m}^2\text{ g}^{-1}$ (Figure 7b). This fact indicates that the inaccessible space in **2G** can now be accessed with N_2 molecules because of the elimination of isopropoxy groups to leave the spaces. Both calcination and acid-treatment basically eliminate isopropoxy groups from **2G**, as confirmed by the disappearance and decrease in the IR bands due to $-\text{CH}_3$

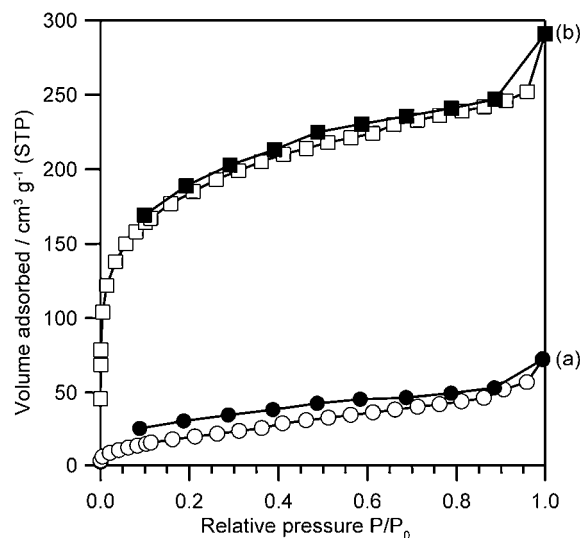


Figure 7. Nitrogen adsorption-desorption isotherms of ethylene-bridged hybrid xerogel **2G** (a) before and (b) after the acid treatment. The open and filled symbols denote adsorption and desorption, respectively.

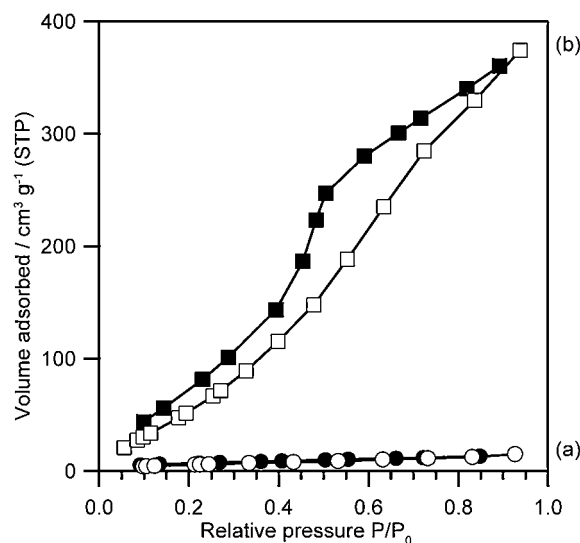


Figure 8. Water adsorption-desorption isotherms of ethylene-bridged hybrid xerogel **2G** (a) before and (b) after the acid treatment. The open and filled symbols denote adsorption and desorption, respectively.

(at 2975 and 2900 cm^{-1} , respectively. Supporting Information, Figure S4). The reason for the lower surface area of calcined **2G** than that of acid-treated **2G** is possibly due to the thermal rearrangement of the siloxane networks accompanied with a partial collapse of D4R framework, as confirmed by the decrease in the band at around 550 cm^{-1} (Supporting Information, Figures S4a and S4c), and the following decomposition of $\text{Si}-\text{CH}_2\text{CH}_2-\text{Si}$ bonding. Furthermore, the water adsorption/desorption isotherms (Figure 8) reveal that the water uptake of **2G** is greatly increased after the acid treatment. This result is attributable to the increase in the pore accessibility of H_2O molecules and to the increase in hydrophilicity of the pore surface. As confirmed by the increase in the IR band at

3652 cm⁻¹ (Supporting Information, Figures S4a and S4b), the ratio of Si–OH groups increased on the pore surface and the effect of a small amount of residual vinyl groups (Figure 6b) should be lowered.

Conclusion

A novel bifunctional siloxane cage, where double four-membered ring (D4R) silicate is capped with alkoxyvinylsilyl groups, was synthesized as a novel building block for the formation of microporous solids. Two different types of microporous networks were obtained either by hydrolysis and polycondensation of alkoxy groups or by hydrosilylation of vinyl groups with H₈Si₈O₁₂, and the resulting materials have uniform distribution of vinyl groups and alkoxy groups, respectively. The vinyl groups contained in the sol–gel-derived xerogel will be useful for post-modification such as bromination, epoxidation, hydroformylation, and metathesis. The xerogel obtained by hydrosilylation showed a significant increase in the surface area upon removal of alkoxy groups by post treatment. Thus the use of such bifunctional nano-building blocks should be very important for the design of novel microporous silica-based materials.

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Supporting Information

Synthesis procedure of **1F**, XRD patterns of **1F** (Figure S1), XRD pattern of **1G** (Figure S2), IR spectra of acid-treated and calcined **1G** (Figure S3), and IR spectra of **2G** (Figure S4). This material is available free of charge on the web at <http://www.csj.jp/journals/bcsj/>.

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