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Building Block Approach to SiO_2–ZrO_2 Porous Materials†

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(2-Hydroxyethyl)trimethylammonium silicate, $Si_8O_{20}[N(CH_3)_3(C_2H_4OH)]_8 \cdot nH_2O$, was allowed to react with zirconium tetrakis(2,4-pentanedionate) in methanol, resulting in gel formation. The gels were heat-treated at 650–1000 °C in air. The product at 650 °C showed a specific surface area of $500\,m^2\,g^{-1}$, and the average pore diameter was *ca* 4.3 nm, indicating the formation of a thermally stable mesoporous body. Gels with the same composition were also prepared by sol–gel processing using tetraethoxysilane as a silica source. The specific surface area of the product yielded by heating the gels at 650 °C was $425\,m^2\,g^{-1}$ and the average pore diameter was *ca* 2.8 nm, which were lower than those of the product from the gels prepared with (2-hydroxyethyl)trimethylammonium silicate. These differences have been attributed to the difference in nanostructure of the gels, caused by the structure of the silica sources and their polymerization behaviour. Copyright © 1999 John Wiley & Sons, Ltd.

Keywords: (2-hydroxyethyl)trimethylammonium silicate; zirconium tetrakis(2,4-pentanedionate); building block approach; trimethylsilylation; SiO_2–ZrO_2; mesoporous materials

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INTRODUCTION

Spherical silicate and silsesquioxane compounds have recently been attracting much attention as raw materials of silica (SiO_2)-based polymeric materials. They can be synthesized facilely by controlled polymerization of silicate anions with organic quaternary ammonium ions[1,2] or hydrolytic condensation of trifunctional silanes.[3] By taking advantage of the unique structures of these compounds, it would be expected to be possible to exert rational control over the nanostructures of the materials.

Some of the main target materials produced from the spherical compounds are porous. Among them, those with the cubeoctameric silicate (Si_8O_{12}) structure have principally been applied for the synthesis. Since the structure corresponds to one of the secondary building units of zeolites,[4] so-called D4R, formation of porous materials from the compounds is feasible provided that the polymerization of the compounds proceeds without the breakdown of the structure. As the first example, Cagle *et al.*[5] demonstrated the production of high-surface-area SiO_2 xerogels by a sol–gel reaction of $Si_8O_{12}(OCH_3)_8$, the methoxide of cubeoctameric silicates. Hoebbel *et al.*[6,7] and Zhang *et al.*[8] reported the synthesis of organic–inorganic hybrid porous materials by hydrosilylation reaction using hydro- and vinyl-dimethylsilyl-functionalized cubeoctameric silicates and silsesquioxanes. We showed the formation of another type of organic–inorganic hybrid porous materials by the reaction of $Si_8O_{20}^{8-}$ with dichlorodimethylsilane.[9–11] These synthesis procedures using this class of compounds have been named the ‘building block approach’.

On the other hand, preparation of multicomponent inorganic porous materials from the cubeoctameric silicate was first reported by Feher and Weller.[12] They conducted the reaction of $Si_8O_{12}(OSnMe_3)_8$ with PCl_3 to obtain P-containing

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SiO_2 porous materials with a surface area of 500 $m^2\,g^{-1}$. The products are notable in terms of the presence of phosphorus(III) therein, since no such compound can be produced by sol–gel processing. However, they are air-sensitive.

Consequently, we have attempted in this study to produce alternative multicomponent inorganic porous materials by the building block approach using the $Si_8O_{20}{}^{8-}$ silicate anion. In our previous paper,[13] we reported that the polymerization of the $Si_8O_{20}{}^{8-}$ anion proceeds without the degradation of its backbone when (2-hydroxyethyl)trimethylammonium silicate, $Si_8O_{20}[N(CH_3)_3(C_2H_4OH)]_8{\cdot}nH_2O$, is just allowed to dissolve in methanol at a SiO_2 concentration of 0.5 mol dm^{-3}. Then, we have investigated on the polymerization process of $Si_8O_{20}{}^{8-}$ in, and gel formation form, methanolic solutions of (2-hydroxyethyl)trimethylammonium silicate by the addition of zirconium tetrakis(2,4-pentanedionate), $Zr(C_5H_7O_2)_4$ (ZTP). Since it was reported that the introduction of a zirconia (ZrO_2) component increases the specific surface area and thermal stability of porous bodies,[14] the ZrO_2 component has been selected to combine with the SiO_2 component in this study. The gels obtained have been heat-treated to convert them into porous materials. In order to compare with these, tetraethoxysilane [$Si(OC_2H_5)_4$, TEOS] and ZTP were used for a sol–gel reaction to prepare gels, with the same amounts of the starting materials as those employed for the reaction of (2-hydroxyethyl)trimethylammonium silicate with ZTP. The gels were calcined under the same conditions, and the properties of the products as porous materials have been compared in terms of the difference in the gel preparation methods.

EXPERIMENTAL

Materials

TEOS, a 50 wt% aqueous solution of (2-hydroxyethyl)trimethylammonium hydroxide, ZTP and methanol were used for preparing samples. Hexamethyldisiloxane, 2-propanol, distilled water, and conc. hydrochloric acid were used for trimethylsilylation of silicate species present in solutions.

Preparation of samples

Solid (2-hydroxyethyl)trimethylammonium silicate was prepared by vigorous stirring of a mixture of 5 cm^3 of TEOS and 5 cm^3 of a 50 wt% aqueous solution of (2-hydroxyethyl)trimethylammonium hydroxide, as was reported previously.[1,15] The solid silicate obtained was purified by recrystallization, i.e. by twice heating the solid over 60 °C to melt it, then cooling.

The purified solid silicate was dissolved in 20 cm^3 of methanol, followed by the addition of ZTP. The methanolic solution was stirred for 10 min at room temperature, and then held at the temperature, resulting in gelation. The gels thus obtained are referred to here as gels formed by the building block approach.

On the other hand, synthesis of gels by sol–gel processing was conducted by mixing simultaneously the same amounts of TEOS, the aqueous solution of (2-hydroxyethyl)trimethylammonium hydroxide, ZTP and methanol as those used for the synthesis by the building block approach. The mixtures were stirred for 10 min at room temperature and then held to obtain gels, which are referred to here as gels formed by sol–gel processing.

In order to remove organic components such as the solvent and (2-hydroxyethyl)trimethylammonium ions involved in these gels, they were dried at 50 °C for over 14 days, and then heat-treated at 650–1000 °C in air. The heating rate was 10 °C min^{-1} and holding time was 1 h. A temperature of 650 °C was necessary for obtaining carbon-free products by heat treatment for 1 h in air.

Analytical procedures

In order to investigate the structures and distribution of silicate species present in the methanolic solutions to give gels, a trimethylsilylation technique by the method of Lentz[16] was employed. The procedure was described previously.[17] The trimethylsilyl derivatives of silicate species obtained were analyzed with a Shimadzu GC-8A gas chromatograph. The analysis conditions were the same as those described elsewhere.[18] Quantitative analysis was conducted on $Si_8O_{20}[Si(CH_3)_3]_8$ using tetradecane as an internal standard.

The XRD patterns of powder samples were recorded on a Rigaku RINT 1100 diffractometer using Ni-filtered Cu K_α radiation.

Measurements for estimating the Brunauer–Emmett–Teller (BET) surface area and pore size distribution of products formed after the heat treatment were conducted at −196 °C with a Carlo Erba Sorptomatic Series 1800 analyzer using N_2 gas as the adsorbate. The samples were pretreated by evacuating for *ca* 2 h at 150 °C.

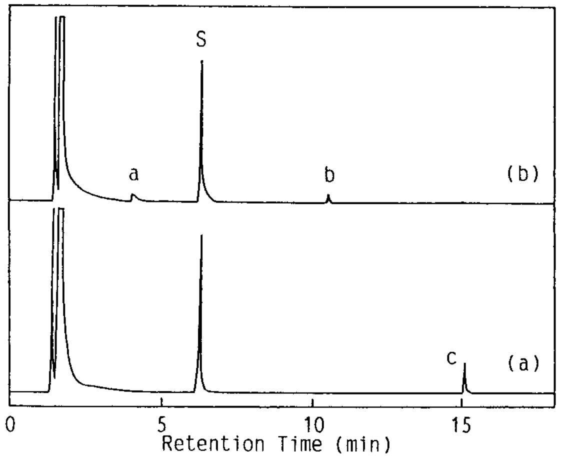

Figure 1 Gas chromatograms of trimethylsilyl derivatives of silicate species present in the methanolic solutions, prepared using (a) (2-hydroxyethyl)trimethylammonium silicate and (b) TEOS as a SiO_2 source, at 10 min of being held at room temperature after 10 min of stirring. Peaks: a, $SiO_4[Si(CH_3)_3]_4$; b, $Si_2O_7[Si(CH_3)_3]_6$; c, $Si_8O_{20}[Si(CH_3)_3]_8$; S, tetradecane (internal standard).

RESULTS AND DISCUSSION

Up to 1.5 g of ZTP could be dissolved in the methanolic solution of (2-hydroxyethyl)trimethylammonium silicate, giving a single-phase solution. When a larger amount of ZTP was added, ZTP precipitated out of the solution. Therefore 1.5 g of ZTP was used in this study. The Si-to-Zr atomic ratio of the solutions is calculated as 7.2.

Gelation took place by holding the methanolic solution containing ZTP for *ca* 1 h at room temperature after 10 min of stirring. The solution without the addition of ZTP did not undergo gelation in such a short reaction time,[13] suggesting that the addition of ZTP caused the gelation of the solution. A solution which was prepared just by mixing TEOS, the aqueous solution of (2-hydroxyethyl)triethylammonium hydroxide, ZTP and methanol gelled at *ca* 50 min of being held at room temperature.

In order to investigate what types of silicate species are present in these solutions prepared by the different methods, the solutions after 10 min of being held at room temperature were submitted to the trimethylsilylation, and the products were analyzed with the gas chromatograph. In the gas chromatogram of the solution prepared by mixing the four kinds of reagents at the same time, trimethylsilyl derivatives of monomeric (SiO_4^{4-}) and dimeric ($Si_2O_7^{6-}$) species gave rise to peaks [Fig. 1(b)]. On the other hand, only one peak was observed at a retention time of 15.2 min, which was due to $Si_8O_{20}[Si(CH_3)_3]_8$, in the gas chromatogram of products obtained from the solution prepared with (2-hydroxyethyl)trimethylammonium silicate [Fig. 1 (a)]. No peaks due to low-molecular-weight silicate species were observed in the gas chromatogram.

The variation in the amount of $Si_8O_{20}^{8-}$ present in the solution as a function of the holding time at room temperature was measured quantitatively with the trimethylsilylation technique, as illustrated in Fig. 2. The amount decreased with the holding time, indicating that polymerization of $Si_8O_{20}^{8-}$ proceeded with time. The presence of low-molecular-weight species was not found in the solution at each holding time, suggesting that the depolymerization of the $Si_8O_{20}^{8-}$ species did not take place in the process of formation of the gel. By comparison with the variation in a methanolic solution of (2-hydroxyethyl)trimethylammonium silicate without the addition of ZTP,[13] it appears that the addition of ZTP actually accelerated the polymerization rate of $Si_8O_{20}^{8-}$. Considering that the $Si_8O_{20}^{8-}$ species in the methanolic solution, where its polymerization rate was rather slow, gave polymeric silicate species without a breakdown of its structure,[13] the $Si_8O_{20}^{8-}$ species in the ZTP-added methanolic solution may also have undergone polymerization with retention of its structure.

On the other hand, the formation of $Si_8O_{20}^{8-}$ was hardly found in the solution prepared by mixing the four reagents simultaneously, although monomeric and dimeric silicate species that were found in the solution as shown in Fig. 1(b) disappeared with holding time to give higher-molecular-weight

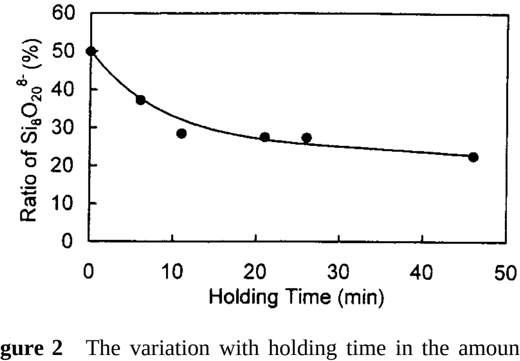

Figure 2 The variation with holding time in the amount of $Si_8O_{20}^{8-}$ in the methanolic solution prepared using (2-hydroxyethy)trimethylammonium silicate as a SiO_2 source. 0 min indicates the time just after the solution had been stirred for 10 min.

Table 1 BET surface areas of SiO_2–ZrO_2 porous materials obtained by heating gels, prepared by the building block approach and sol–gel processing, at various temperatures for 1 h in air

	BET surface area (m^2/g^{-1})	
Heating temperature (°C)	Gels produced by the building block approach	Gels produced by sol–gel processing
650	500	425
800	434	376
900	324	260
1000	188	161

silicate species. This suggests that silicate species in the solution underwent random polymerization.

Briefly, the $Si_8O_{20}{}^{8-}$ silicate anion in the ZTP-added methanolic solution of (2-hydroxyethyl)trimethylammonium silicate polymerized without the depolymerization, resulting in gel formation. Also, the polymerization rate was considerably accelerated by the addition of ZTP. In the solution prepared by mixing the four reagents simultaneously, hydrolysis products of TEOS were formed randomly.

The gels thus obtained were dried at 50 °C for over 14 days to make their weights constant by removing the solvent entrapped in the gels. Then they were heat-treated at 650–1000 °C in air for 1 h, yielding white powders consisting of SiO_2 and ZrO_2 components. The specific surface area of the powders is shown in Table 1.

The SiO_2–ZrO_2 powders formed by heating the gels prepared by the building block approach at 650 °C reveal a BET surface area of 500 m^2 g^{-1}. Their pore size distribution is shown in Fig. 3. The pore diameter was over 2 nm and the average pore diameter was *ca* 4.3 nm, indicating the formation of mesoporous materials.

The gels were also heated at 650 °C for 1 h at various heating rates from 2 to 10 °C min^{-1}. The specific surface area of the resulting powders was 495–527 m^2 g^{-1}. However, no relationship has been found between the heating rate and the specific surface area of the powders. The areas of powders obtained on the other runs were also within this range, suggesting that such a difference in the specific surface area would be inherent in this synthesis procedure.

The specific surface area of the porous bodies decreased with increasing heating temperature, as shown in Table 1. Their XRD patterns are illustrated in Fig. 4. A broad peak is seen, centered around 22° in the pattern of the powders obtained by calcining at 650 °C [Fig. 4 (a)], indicating that they are amorphous. With increasing heating temperature, the other broad peaks are observed around 30° and 50°. Pirard *et al.* reported that tetragonal ZrO_2 crystallizes upon heating SiO_2–ZrO_2 aerogels with a Zr content of 80 mol% over 400 °C.[19] From this fact and the diffraction angles, the appearance of the two broad peaks would result from the crystallization of the ZrO_2 component in the products. Such structural changes in the porous bodies would lead to the decrease in the specific surface area. Nevertheless, the powders obtained by

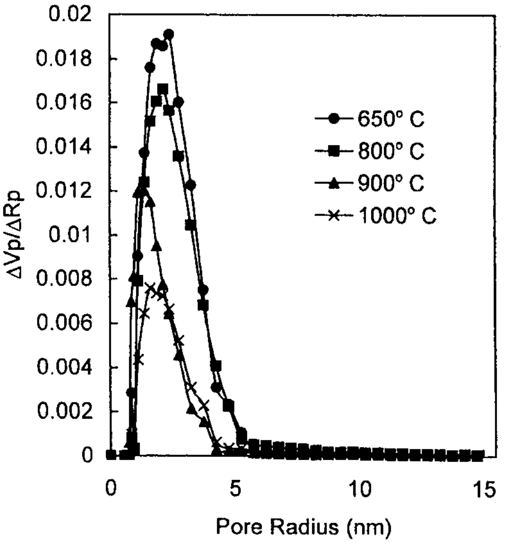

Figure 3 Pore size distribution of SiO_2–ZrO_2 porous bodies obtained by heating gels prepared from (2-hydroxyethyl)trimethylammonium silicate as a SiO_2 source at 650 (●), 800 (■), 900 (▲), and 1000 °C (×) in air for 1 h.

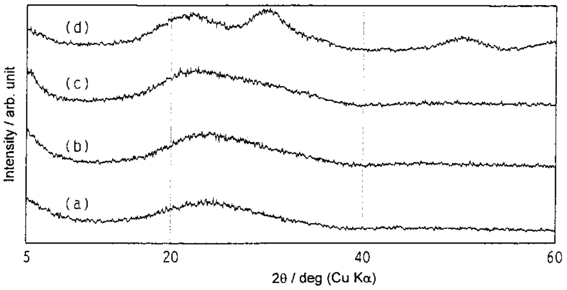

Figure 4 XRD patterns of SiO_2–ZrO_2 porous bodies synthesized by calcining gels prepared from (2-hydroxyethyl)trimethylammonium silicate as a SiO_2 source at (a) 650, (b) 800, (c) 900 and (d) 1000 °C in air for 1 h.

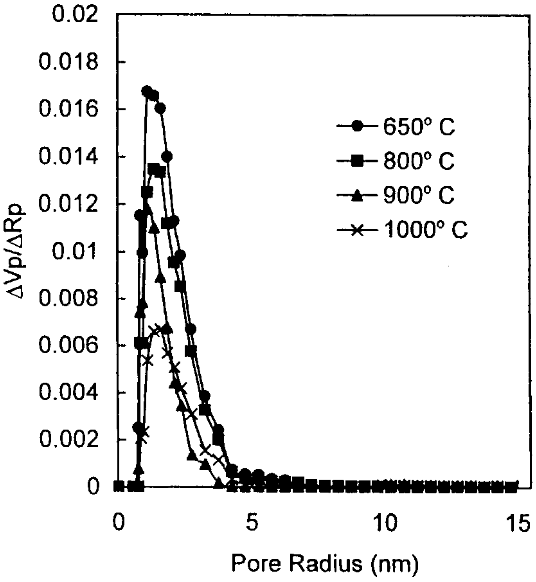

Figure 5 Pore size distribution of SiO_2–ZrO_2 porous bodies produced by firing gels prepared from TEOS as a SiO_2 source at 650 (●), 800 (■), 900 (▲), and 1000 °C (×) in air for 1 h.

the heat treatment at 800 °C still revealed a surface area of 434 m^2g^{-1}, which was much higher than that of $Si_8O_{20}{}^{8-}$-derived silica gels calcined at that temperature (200 m^2g^{-1}) (I. Hasegawa and K. Hibino, unpublished results). This supports that the introduction of the ZrO_2 component improves the thermal stability of porous bodies, which was earlier reported by Lopez *et al.*[14]

XRD patterns of the white powders obtained from the gels prepared by sol–gel processing reveal the same profiles as those seen in Fig. 3, indicating that the products are also amorphous and the crystallization of the ZrO_2 component takes place by firing at higher temperatures. Their specific surface areas are shown in Table 1 as well. The powders obtained by the heat treatment at 650–900 °C show lower surface areas than those produced by the building block approach, while there is no significant difference with the gel preparation methods in the area of the powders formed at 1000 °C. This would be attributed to structural changes occurring at such a very high temperature as that being observed with the XRD analysis.

The pore size distribution of SiO_2–ZrO_2 powders prepared by sol–gel processing is shown in Fig. 5. The pore diameters are more than 2 nm, indicating that these are also mesoporous bodies. However, the average pore diameter of the powders formed after the heat treatment at 650 and 800 °C is *ca* 2.8 nm, which is smaller than that of the powders prepared by the building block approach.

The (2-hydroxyethyl)trimethylammonium ion, which is present in both of the reaction systems, was demonstrated to act as an organic template in zeolite synthesis.[20] Therefore, the ion would play the similar role in the formation of the SiO_2–ZrO_2 amorphous porous bodies. Nevertheless, it is clear that the surface area of the products formed by heating the gels derived by the building block approach at 650–900 °C is even higher than that obtained by sol–gel processing. There is also a difference in the pore size distributions.

Whether the $Si_8O_{20}{}^{8-}$ structure is fully preserved during the heat treatment is still obscure. Considering that structural changes caused by the heat treatment would take place to almost the same degree in the gels produced by these two methods, however, the difference in the surface area and pore size distribution of the resulting powders would be attributable to that in the nanostructures of the gels. The formation of the nanostructures would be affected by the structures of the SiO_2 source, $Si_8O_{20}{}^{8-}$ and $SiO_4{}^{4-}$, and their polymerization behaviour. This would suggest that control over nanostructures by the building block approach is also effective for the synthesis of materials for which heat treatment at high temperatures is required.

CONCLUSIONS

SiO_2–ZrO_2 mesoporous bodies were synthesized by two different methods. SiO_2–ZrO_2 gels prepared from the compound with the $Si_8O_{20}{}^{8-}$ structure as a SiO_2 source gave porous powders with a specific surface area of 500 m^2g^{-1} and an average pore diameter of *ca* 4.3 nm after heat treatment at 650 °C, whereas gels produced using TEOS as a SiO_2 source gave powders with a lower surface area and a smaller average pore diameter by the heat treatment. These differences were considered to result from the difference in nanostructures of their precursor gels leading from the structure of the SiO_2 sources and their polymerization behaviour.

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