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Preparation of Porous Acidic Oxides from Group 13
Element-containing Oligosilsesquioxanes

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The controlled calcination of newly-synthesized group 13 element-containing silsesquioxanes, $\text{PhB}[(\text{Me}_3\text{SiO})(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}]$ **1** and $[\text{PPN}]^+\{\text{Ga}[(\text{Me}_3\text{SiO})(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}]_2\}^-$ **3b**, as well as $[\text{HNEt}_3]^+\{\text{Al}[(\text{Me}_3\text{SiO})(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}]_2\}^-$ **2**, $[\text{HNEt}_3]^+\{\text{Ga}[(\text{Me}_3\text{SiO})(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}]_2\}^-$ **3a**, and $[\text{C}_{14}\text{H}_{18}\text{N}_2\text{H}]^+[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{GaCl}]^-$ **4** at around 823 K produces acidic oxides with high BET surface areas of 330–520 $\text{m}^2 \text{g}^{-1}$ and uniformly-controlled micropores of 5.1 Å diameter. Detailed investigation of these oxides revealed that the pore structures are not greatly influenced by the presence of the group 13 elements and counter cations. However, the acidic properties are greatly affected by the structure of the silsesquioxane precursors, and partly controlled by the group 13 elements and counter cations. In particular, oxides from **2**, **3a** and **3b** were found to have high BET surface areas and large numbers of acidic sites. The oxides from **3a** have relatively strong acidic sites, whereas oxides from **2** and **3b** have weak and moderate strength acidic sites. The oxides from **4** do not show significant surface acidity. Differences in the dispersion of the oxides of group 13 elements in the silica matrixes, which are closely related to the structure of precursors, are considered partly account for the differences in acidic character.

Keywords

Silsesquioxane, Gallium, Aluminum, Boron, Microporous oxide, Solid acidic catalyst

1. Introduction

Group 13 element-containing oxides such as silica-alumina, aluminosilicates, gallosilicates, and borosilicates have been extensively studied because of their great importance in current chemical industries and petroleum refineries, mainly as solid acidic catalysts¹⁾. Therefore, development of novel solid acidic oxide materials with well-defined pore structures and controlled acidic characters is of great significance.

Metal-containing oligosilsesquioxanes with cubic core structures provide well-defined, homogeneous models for the active surface sites of supported catalysts or metal-containing zeolites^{2)–22)}, as well as incompletely condensed oligomers with silanol groups as models of silica^{23)–27)}. The chemistry of corner-capped type metallasilsesquioxanes has been established²⁾, and heterosiloxanes that can be regarded as models for zeolites³⁾ has been developed. Several silsesquioxanes containing gallium⁸⁾, aluminum^{9)–14)}, or boron^{15),16)} have also been synthesized.

Metal-containing silsesquioxanes have been examined not only as *homogeneous* catalysts^{5),6),16)–22)} but also as precursors for the preparation of *heterogeneous*

catalysts^{5),6),12),28)–31)}. For example, aluminum-containing silsesquioxane gels prepared from aluminum tributoxide and silsesquioxane disilanol are active catalysts for Diels–Alder reactions¹²⁾. We previously reported excellent activities of the oxide catalysts prepared from a silica-supported vanadium-containing silsesquioxane in the selective photo-assisted oxidation of methane into methanal²⁹⁾. The resulting oxide catalysts possessed markedly larger specific surface areas than the parent silica supports. In addition, we found that a titanium-containing silsesquioxane is a convenient precursor for Ti–Si–O materials with high surface areas and uniformly-controlled micropores³⁰⁾. Subsequently, preparation of microporous oxides from chromium-containing silsesquioxanes and their catalytic activities were reported³¹⁾. Therefore, acidic mixed oxides with controlled pore structures could be produced from silsesquioxanes containing a group 13 element in the siloxane framework. Note that acidic oxide catalysts active for, e.g., 1-butene isomerization have been made by the calcination of incompletely condensed silsesquioxane, $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OH})_3$ **6**, supported on alumina³²⁾.

The present study extended our methodology for the preparation of porous oxides to group 13 element-containing silsesquioxanes. Novel gallium and boron-

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containing silsesquioxanes were synthesized. These silsesquioxanes, as well as similar compounds previously reported, were processed by careful calcination in an air stream to produce microporous oxides with controlled acidity and pore structure. The effects of precursor molecules and calcination conditions on the pore structures and acidic characters of the resulting oxides were evaluated by various spectroscopic methods. Preliminary results were reported previously³³.

2. Experimental Section

2.1. Materials

1,3,5,7,9,11,14-Heptacyclopentyltricyclo[7.3.3.1^{5,11}]heptasiloxane-*endo*-3,7,14-triol **6**, dichlorophenylborane, and trimethylaluminum in hexane solution (1 M) were purchased from Aldrich and used as received. Organic solvents such as hexane, benzene, toluene, tetrahydrofuran (THF), diethyl ether, and triethylamine were carefully distilled using appropriate drying reagents just before use. Other organic reagents were delivered from Wako Pure Chemical Industries, Ltd. and Nacarai Tesque Co. and used without further purification. The detailed synthetic procedure for the gallium-containing silsesquioxane **3a** was reported elsewhere³³. An aluminum-bridged silsesquioxane **2**¹⁴ and a corner-capped type gallium-containing silicate complex **4**⁸ were prepared according to known literature procedures.

2.2. Preparation of **1**

All synthetic procedures of group 13 element-containing silsesquioxanes were carried out under an argon atmosphere by standard Schlenk techniques. Silsesquioxane disilanol (*c*-C₅H₉)₇Si₇O₉(OSiMe₃)(OH)₂ **5**³⁴ (473 mg, 0.50 mmol) and triethylamine (0.3 cm³, 2.2 mmol) were dissolved in dry toluene (10 cm³), then dichlorophenylborane (80 mg, 0.50 mmol) in dry toluene (10 cm³) was added dropwise and stirred at room temperature for 24 h. After the solvent was evaporated, the resulting off-white solid was extracted with hexane (10 cm³). Filtration through a glass filter (G4) gave a clear solution. After evaporation, colorless microcrystals of a boron-containing silsesquioxane **1** were obtained by recrystallization through slow diffusion of acetone into a benzene solution. Yield 70%. M.p. 238.5–239.0°C; ¹H NMR (300 MHz, CDCl₃, 25°C); δ 7.85–7.31 (br m, 5H, Ph), 1.89–1.52 (br m, 56 H, CH₂ of Cy (*c*-C₅H₉)), 1.19–0.89 (br m, 7H, CH of Cy), –0.11 (s, 9H, Si(CH₃)₃); ¹³C{¹H}NMR (75 MHz, CDCl₃, 25°C); δ 135.64, 130.90, 127.33 (Ph), 27.55, 27.47, 27.32, 27.27, 27.16, 27.06, 26.99, 26.97 (CH₂ of Cy), 23.92, 23.03, 22.85, 22.34, 22.04 (1 : 2 : 2 : 1 : 1 for CH of Cy), 1.41 (Si(CH₃)₃); ²⁹Si{¹H}NMR (76 MHz, CDCl₃, 0.2 M Cr(acac)₃, 25°C) δ 9.06, –63.69, –64.88, –66.90, –67.76 (1 : 1 : 1 : 1 : 4). MS (FAB) *m/z* 1017 (13) [M–CH₃]⁺, 963 (100) [M–C₅H₉]⁺. Anal.

Calcd for C₄₄H₇₇BO₁₂Si₈ (1033.57): C, 51.13; H, 7.51. Found C, 50.01; H, 7.45%.

2.3. Preparation of **3b**

A solution of **3a** (1095 mg, 0.53 mmol) and bis(triphenylphosphoranylidene)ammonium chloride (PPNCl, 305 mg, 0.53 mmol) in dry benzene (10 cm³) and acetone (20 cm³) was stirred at room temperature for 24 h. After the solvent was evaporated, 2 cm³ of dry benzene and 60 cm³ of hexane were added to the resulting solid. After vigorous stirring for 1 h, filtration through a glass filter (G4) gave a clear solution. After evaporation, the resulting white solid was washed with methanol (10 cm³ × 3), followed by vacuum drying. Colorless crystals of **3b** were obtained by recrystallization through slow diffusion of hexane into a chloroform solution. Yield 60%. M.p. 183.0–184.0°C; ¹H NMR (300 MHz, CDCl₃, 25°C) δ 7.73–7.36 (m, 30H, Ph of PPN⁺), 1.68–1.26 (br m, 112H, CH₂ of Cy), 0.90–0.82 (br m, 14H, CH of Cy), 0.09 (s, 18H, Si(CH₃)₃); ¹³C{¹H}NMR (75 MHz, CDCl₃, 25°C) δ 134.12–129.63 (m, Ph of PPN⁺), 28.31, 28.27, 28.09, 27.80, 27.76, 27.73, 27.53, 27.31, 27.28, 27.19, 27.16, 27.10, 27.02, 26.97 (CH₂ of Cy), 25.81, 24.97, 24.67, 24.05, 23.92, 23.02, 22.97 (1 : 1 : 1 : 1 : 1 : 1 : 1 for CH of Cy), 2.06 (Si(CH₃)₃); ²⁹Si{¹H}NMR (76 MHz, CDCl₃, 0.2 M Cr(acac)₃, 25°C) δ 9.63, –65.22, –65.64, –67.02, –67.09, –69.80, –69.95 (1 : 2 : 1 : 1 : 1 : 1 : 1). Satisfactory microanalytical data could not be obtained because of severe formation of carbidic species during the combustion analysis. Anal. Calcd for C₁₁₂H₁₇₄NO₂₄GaSi₁₆P₂ (2499.66): C, 53.82; H, 7.02; N, 0.56%. Found C, 52.08; H, 7.00; N, 0.52%.

2.4. Preparation of Oxides from Silsesquioxanes

Calcination of group 13 element-containing silsesquioxanes (typically 0.50 g) was performed in a stream of dried, CO₂-free air (*W/F* = 5.0 g h mol^{–1}) using a fixed-bed flow type quartz reactor (i.d. 8.0 mm) under atmospheric pressure. Temperature was raised by 10 K min^{–1} to the prescribed level, and maintained for 4 h. Calcined samples were carefully recovered with minimal contact with air and moisture, and stored under an argon atmosphere.

2.5. Analysis

Liquid NMR data were mainly obtained with a JEOL JNM-AL300 spectrometer operating at 300 and 75 MHz for ¹H and ¹³C, respectively. The ²⁹Si NMR data were obtained using a JEOL JNM-EX400 spectrometer operating at 76 MHz. Chemical shifts are reported relative to tetramethylsilane. Fast atomic bombardment (FAB) mass spectra of silsesquioxanes were recorded using a JEOL SX-102A mass spectrometer. 2-Nitrophenyl octyl ether was used as the matrix. Elemental analyses were performed at the Microanalytical Center of Kyoto University. TG and DTA analyses were done using a Shimadzu DTA-50 analyzer in a stream of synthesized air or dry nitrogen (40 cm³ min^{–1} for typi-

cally 15 mg of silsesquioxanes).

The resulting oxides were analyzed by nitrogen gas adsorption, XRD, DRIFTS, XPS, SEM, EPMA, ammonia TPD and other methods. Nitrogen adsorption/desorption isotherms were obtained with a Quantachrome Autosorb 1-MP, a computer-controlled automatic gas sorption system. Samples were degassed at 473 K for 2 h just before the measurements. XRD (X-ray diffraction) was performed using a Shimadzu XD-D1 with $K\alpha_{1,2}$ -emission of copper in the range $5^\circ < 2\theta < 70^\circ$. DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) measurements were performed with a Nicolet MAGNA-IR 560 equipped with a Spectra-Tech DRIFT attachment. The samples were held in a flow of He ($40 \text{ cm}^3 \text{ min}^{-1}$) at 573 K for 1 h, and pyridine vapor was allowed to flow over the samples at 373 K for 1 h. After physically adsorbed pyridine molecules were removed at 573 K for about 3 h, FTIR spectra were recorded. All spectra were modified with the Kubelka-Munk function. XPS (X-ray photoelectron spectra) of the catalysts were acquired using an ULVAC-PHI 5500MT system equipped with a hemispherical energy analyzer. Samples were mounted on indium foil and then transferred to an XPS analyzer chamber. The residual gas pressure in the chamber during data acquisition was less than 1×10^{-8} Torr ($1 \text{ Torr} = 133.3 \text{ N m}^{-2}$). The spectra were measured at room temperature using Mg $K\alpha_{1,2}$ radiation (15 kV, 400 W). The electron take-off angle was set at 45 deg. Binding energies were referenced to C 1s level of residual graphitic carbon. The apparent shape and size of the oxide particles were assessed using a Hitachi S-2500 CX scanning electron microscope (SEM). EPMA analyses were performed using a spot energy differential X-ray analyzer, HORIBA EMAX 5770.

Temperature-programmed desorption (TPD) of ammonia was measured using a TPD-1-AT apparatus (Bel Japan, Inc.). The samples were pretreated at 723 K for 1 h in a stream of He ($50 \text{ cm}^3 \text{ min}^{-1}$). After ammonia gas was allowed to flow into the sample holder at 373 K, $2.7 \times 10^3 \text{ N m}^{-2}$ for 10 min, ammonia was evacuated for 1 h, followed by TPD measurement using a Q-mass detector from 373 K to 873 K (10 K min^{-1}). Mass number 16 was monitored to evaluate the amount of desorbed ammonia. A longer evacuation period up to 13 h at 373 K just after ammonia adsorption did not significantly change the TPD spectra. The sensitivity to ammonia was calibrated just after each experiment.

3. Results and Discussion

3.1. Preparation of Group 13 Element-containing Silsesquioxanes

Reaction of dichlorophenylborane with an equimolar amount of silsesquioxane disilanol **5** in the presence of excess triethylamine in toluene solution at room tem-

perature for 24 h formed a boron-containing silsesquioxane **1** with a yield of 70% (Eq. (1)). The

structure of **1** was deduced on the basis of ^1H , ^{13}C and ^{29}Si NMR, and FAB-MASS spectra. The ^{13}C NMR spectrum indicated the presence of one phenyl group directly bound to the boron atom, and five resonances in a 1 : 2 : 2 : 1 : 1 ratio for the *ipso*-carbon atoms in the cyclopentyl rings, which is consistent with the local C_s symmetry of the siloxane framework. In addition, there was no sign of the coordination of amines or solvents by ^1H NMR. These results indicate structure **1** shown in Eq. (1). More detailed structural analysis is now proceeding.

Gallium-bridged silsesquioxane **3a** was obtained in 69% yield by the reaction of gallium trichloride with two equivalents of **5** in the presence of excess triethylamine in benzene-diethyl ether solution at room temperature for 24 h, as reported previously (Eq. (2))³³.

To investigate the effects of the counter cation on the nature of the resulting oxides, a PPN (bis(triphenylphosphoranylidene)ammonium) salt **3b** was prepared by the cation exchange of **3a** with PPNCl in benzene-acetone (Eq. (3)). The ^1H NMR spectrum of **3b** clearly showed the presence of two half-cage silsesquioxane cores and one PPN⁺ cation in the molecule. The ^{29}Si NMR spectrum consisted of eight peaks of almost the same intensity for sixteen silicon atoms, which indicated apparent local C_2 -symmetry of the siloxane frame-

work of **3b**. These spectroscopic results of **3b** are in good accordance with the data reported for triethylammonium salt **3a**³³⁾ or $[\text{HNEt}_3]^+ \{ \text{Al}[(\text{Me}_3\text{SiO})(c\text{-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{11}]_2 \}^-$ ¹³⁾.

A cyclopentyl derivative of a known corner-capped type gallium-containing silsesquioxane⁸⁾, $[\text{C}_{14}\text{H}_{18}\text{N}_2\text{H}]^+ [(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{GaCl}]^-$ **4**, was synthesized for comparison. An aluminum-bridged silsesquioxane **2** was also prepared *via* the synthetic route reported before (Scheme 1)¹⁴⁾.

3.2. Characterization of the Oxides Prepared from Group 13 Element-containing Silsesquioxanes

Since group 13 elements in the silsesquioxanes described above are atomically dispersed, these elements are expected to be bonded or at least stay close

Scheme 1

to the siloxane cages even under an oxidizing atmosphere at high temperature^{30,31)}, so controlled calcination of group 13 element-containing silsesquioxanes was performed.

First, analyses by TGA and DTA of group 13 element-containing silsesquioxanes were performed in an air stream to investigate the effects of temperature on the decomposition of the organic moiety during calcination (Fig. 1). For the boron-containing silsesquioxane **1**, the observed weight decrease was consistent with that expected (50.1%). Since a large amount of carbidic carbon was identified on the surface of the oxide from **1** in the XPS study (*vide infra*), the formation of the carbidic carbonaceous species should be taken into account. In contrast, TG measurement of **2** found a slightly endothermic weight loss of *ca.* 5%, probably due to the decomposition of the ammonium cation, at around 473 K. Subsequently, a significant exothermic weight decrease corresponding to combustion of the cyclopentyl rings occurred at around 700 K. However, the total mass decrease (58.7%) exceeded the theoretical decrease (49.9%) taking into account the complete combustion of the cyclopentyl and methyl groups. Similar weight decreases over the theoretical value, which indicate partial loss of the inorganic moiety or partial sublimation of silsesquioxane during the calcination, were also observed for **3a** and **3b** (theoretical decreases of 48.9% and 52.1%, respectively). The TG profile of **3a** was very similar to that of **2**. Gradual weight loss of **3b** started at around 573 K, higher than with **3a**, indicating the higher thermal stability of **3b**. The weight loss of **4** was barely larger than the theoretical value (56.9%). Since weight loss

Fig. 1 TG Analysis of Silsesquioxanes in a Stream of Synthesized Air

Table 1 BET Surface Areas of the Oxides^{a)}

Samples ^{b)}	BET surface area [m ² g ⁻¹]	Total pore volume [cm ³ g ⁻¹]
1-823	330	0.11
2-723	520	0.23
2-823	460	0.20
2-923	360	0.16
3a-723	400	0.18
3a-823	410	0.20
3a-923	330	0.17
3b-823	410	0.20
4-823	410	0.21
6-823	420	0.18
6-823 ^{c)}	300	0.13

a) All samples were evacuated at 473 K for 2 h just before the measurement.

b) Numbers represent the calcination temperature (K).

c) Treated under 23.8 Torr of water vapor at 298 K for 7 days.

exceeding the expected value is commonly observed for trimethylsilyl-substituted silsesquioxanes except for **1**, partial loss of the trimethylsilyl groups may be responsible.

Calcination of **1**, **2**, **3a**, **3b**, and **4** in an air flow for 4 h produced microporous M-Si-O materials (M = B, Al, Ga). The oxide derived from **1** at 823 K was further designated as 1-823. **Table 1** summarizes the specific surface areas and total pore volumes of the oxides. The surface area of the oxides from silsesquioxane **6**, which does not contain any group 13 elements, were also measured for comparison. Calcination of the silsesquioxanes at temperature below 623 K produced black solids with small specific surface areas of less than 2 m² g⁻¹. Optimum calcination temperature to produce oxides with surface areas of 330-520 m² g⁻¹ was 723-823 K. Higher temperatures significantly decreased the surface areas. In particular, 2-723 and 2-823 showed the highest BET surface areas of 520 m² g⁻¹ and 460 m² g⁻¹, respectively, whereas oxides from **1** had smaller surface areas. Oxide **3b**-823 had the same surface area as **3a**-823, indicating that surface areas are not affected by the cationic species at all. To investigate the stability of the pore structure against moisture, **6**-823 was treated at 298 K for 7 days in the presence of 23.8 Torr of water vapor (argon balance). As shown in **Table 1**, the surface area of the treated **6**-823 was significantly lower than that of the untreated sample, indicating the instability of these microporous structures in the presence of water vapor.

Figure 2 shows the nitrogen adsorption isotherms of the oxides produced at 823 K. Typical type-I isotherms, characteristic of microporous materials³⁵⁾, were observed except for **4**-823, which showed a steep increase in adsorption at low P/P_0 together with a gradual increase at P/P_0 over 0.1, indicating a broader pore size distribution. Both untreated **6**-823 and water

Fig. 2 Nitrogen Adsorption Isotherms of the Oxides (a) 1-823, (b) 2-823, (c) 3a-823, (d) 3b-823, and (e) 4-823

Fig. 3 Pore Size Distribution of the Oxides (a) 1-823, (b) 2-823, and (c) 3a-823 Calculated on the Basis of Nitrogen Adsorption Isotherms by the Saito-Foley Method

vapor-treated **6**-823 also showed type-I isotherms. The isotherm of **3b**-823 completely coincided with that of **3a**-823. Again, no influence of the bulky cationic species (PPN⁺ versus HNEt₃⁺) was observed, probably due to the complete loss of the HNEt₃⁺ or PPN⁺ cation during the heating stage before the formation of micropores started by the combustion of cyclopentyl groups.

Figure 3 shows the pore size distribution of 1-823, 2-823 and 3a-823 derived from the nitrogen adsorption isotherms measured by the Saito-Foley method using the sorbent parameters for the oxide ions of zeolites³⁶⁾. All plots revealed a sharp peak at a pore diameter around 5.1 Å. There was no sign of mesopore forma-

Table 2 XPS Analysis of the Oxides Prepared from Group 13 Element-containing Silsesquioxanes

Samples	Group 13 element [M]	Surface composition [atom %]				Si/Me	Binding energy [eV]		
		M	Si	O	C		This work	(Ref. ^{a)})	
1-823	B	4.1	26.1	52.5	17.4	6.5	B 1s	193.4	(192.0)
2-823	Al	2.1	27.4	62.2	8.3	13	Al 2p	75.0	(74.0)
3a-823	Ga	1.1	30.7	61.7	6.5	28	Ga 2p _{3/2}	1119.1	(1116.9)
3b-823 ^{b)}	Ga	2.1	24.6	58.8	11.8	12	Ga 2p _{3/2}	1119.2	

a) Binding energy of M₂O₃ (M = B, Al, Ga) reported in the literature (Ref. 38)).

b) In addition to Ga, Si, O and C, 2.7 atom % of P was observed.

tion. Pore textures of the oxides synthesized in the present study were very similar to those observed in the oxides produced from titanium-³⁰⁾, chromium-³¹⁾, or zirconium-containing silsesquioxanes³⁷⁾, indicating that the characteristic pore textures comparable to those of MFI-type zeolites³¹⁾ are not greatly affected by the metallic species. Since the results of TG and nitrogen adsorption show that the temperature required for the formation of micropores is just above the temperature for complete oxidation of cyclopentyl groups bonded to silicon atoms (*vide supra*), formation of new Si-O-Si bonds accompanied by oxidative decomposition of the peripheral organic groups is considered to be mostly responsible for the formation of uniform micropores. Therefore, the pore structure would mainly depend on the half-caged organosilsesquioxane moieties, and would not be significantly affected by the metallic species and counter cations. Further detailed spectroscopic study is continuing.

EDX analyses of 3a-823 and 3b-823 showed a Si/Ga ratio of 15, slightly lower than that of 3a or 3b (Si/Ga = 16). Similar results were obtained for 2-823 (Si/Al = 15). The oxide 4-823 showed a slightly lower Si/Ga ratio (6.7) to that of 4 (Si/Ga = 7.0). However, accurate measurement of the bulk Si/B ratio in 1-823 has not been achieved.

The XRD spectra of all the oxides calcined at 823 K consisted of only one broad band at around $2\theta = 23$ deg. This indicates that all the oxides are amorphous.

Table 2 summarizes the results of the XPS study. The atomic ratios were calculated based on the sensitivity factors reported for the spectrometer used in this study³⁸⁾. The surface of 1-823 consists of 4.1 mol% of boron and 26.1 mol% of silicon atoms together with 17.4 mol% of both carbidic and graphitic carbon (*ca.* 1 : 2), indicating the incorporation of boron atoms onto the oxide surface in the Si/B ratio of 6.5. The ratio of Si/Al on the surface of 2-823 was 13, slightly lower than the bulk ratio (15). The Al 2p peak was significantly shifted towards the higher binding energy side (75.0 eV) from the reported value for γ -Al₂O₃ (74.0 eV)³⁸⁾. Similar shifts towards high binding energy were also observed for B 1s in 1-823 and Ga 2p_{3/2} in 3a-823 and 3b-823. These phenomena have been

Fig. 4 Ammonia-TPD Profiles of the Oxides (a) 1-823, (b) 2-823, (c) 3a-823, (d) 3b-823, (e) 4-823, and (f) 6-823

reported for titanosilicates or silica-titania catalysts and assigned to the elements surrounded by electron-withdrawing siloxane frameworks^{30),39)}. In the thin layer of silica deposited on alumina, similar shifts have been considered to be responsible for the Al-O-Si bonds in high dispersion⁴⁰⁾. The surface Si/Ga ratio of 3a-823 was significantly higher at 28, suggesting a lower dispersion of group 13 elements in 3a-823 than in 2-823 as discussed before for supported molybdenum catalysts^{41),42)}. The surface atomic ratio of Si to Ga of 3b-823 was markedly lower than that of 3a-823, indicating that differences of counter cation significantly influence the dispersion of Ga species on the surface of the resulting oxides, although the exact reason is still unclear. In addition, the presence of a residual phosphorus species was observed on the surface of 3b-823, whereas there was no sign of residual nitrogen.

Investigation on the solid acidic characters of the oxides calcined at 823 K by temperature-programmed desorption (TPD) of ammonia is summarized in Fig. 4. The results for 6-823 prepared from a silsesquioxane trisilanol 6 are also presented for comparison. The TPD spectrum of 1-823 consists of a broad desorption

Fig. 5 FTIR Spectrum of Pyridine Adsorbed on the Surface of **3a**-823

band at around 450 K, indicating the presence of only weak acidic sites. Total amount of desorbed ammonia was $0.131 \text{ mmol g}^{-1}$. In contrast, **2**-823 exhibited two bands at around 473 K and 573 K, suggesting the presence of both weak and moderate strength acidic sites. Similar TPD spectra have often been reported for conventional silica-alumina catalysts⁴³. This sample desorbed $0.289 \text{ mmol g}^{-1}$ of ammonia, corresponding to about one-third of the amount of aluminum included in the oxide. The TPD spectra of **3a**-823 consisted of three broad desorption bands at around 450, 575, and 720 K. This indicates the presence of stronger acidic sites than HZSM-5 (Si/Al = 20), since the measurement of HZSM-5 under identical conditions showed two bands at 450 K and 620 K. Such strong acidic sites are considered to be characteristic of gallium-containing siliceous catalysts including mesoporous gallium-containing silicas, GaMCMs⁴⁴. This **3a**-823 desorbed a large amount of ammonia ($0.343 \text{ mmol g}^{-1}$), although the XPS analysis suggested the formation of clusters of gallium species. The band at 720 K was not observed for **3b**-823, which also desorbed a large amount of ammonia ($0.327 \text{ mmol g}^{-1}$). Since the presence of phosphorous atoms on its surface was shown by the XPS study (*vide supra*), poisoning of strongly acidic sites by the residual phosphorous species derived from the PPN⁺ cation is considered to be responsible. In contrast, **4**-823 desorbed a significantly smaller amount of ammonia (less than $0.050 \text{ mmol g}^{-1}$) in spite of its larger content of gallium species than **3a**-823.

Investigation by FTIR of pyridine adsorbed on the gallium-containing oxide, **3a**-823, was performed to discriminate Lewis and Brønsted acidic sites (Fig. 5). The spectrum showed a strong band at around 1530 cm^{-1} together with a weak band at 1450 cm^{-1} . The absorption peak at around 1530 cm^{-1} was assigned to the pyridinium ion formed by interaction with Brønsted acid sites, although the observed band was slightly shifted toward lower wavenumbers compared with

those usually reported⁴⁵, but the reason of such shift is unclear. On the other hand, the weak peak at around 1450 cm^{-1} was located between the values assigned to physically adsorbed pyridine and pyridine coordinated to Lewis acidic sites⁴⁵. The present FTIR measurements distinctly indicate the predominant formation of Brønsted acidic sites on the accessible surface.

The SEM and EPMA mapping measurements of **3a**-823 and **4**-823 revealed differences in the distribution of the gallium species on their surfaces. In the case of **4**-823, formation of large (*ca.* $10 \mu\text{m}$), discrete particles of gallium species was observed. In the case of **3a**-823, the distribution of Si and Ga species roughly coincided, and there was no sign of the formation of very large particles of gallium oxide observable by EPMA analysis (in the present case, $> 0.1 \mu\text{m}$). Marked differences in the dispersion of the gallium species between **4**-823 and **3a**-823 could account for the observed variations in the acidic characters. The relatively low stability of **4** towards water vapor compared with **3a** would result in complete separation of the gallium species from the siloxane matrix during calcination.

4. Conclusion

Porous M-Si-O materials (M = B, Al, Ga) with solid acidity were produced by the controlled calcination of a series of novel group 13 element-containing silsesquioxanes, $\text{PhB}[(\text{Me}_3\text{SiO})(\text{c-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}]$ **1** and $[\text{PPN}]^+\{\text{Ga}[(\text{Me}_3\text{SiO})(\text{c-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}]_2\}^-$ **3b**, as well as $[\text{HNEt}_3]^+\{\text{Al}[(\text{Me}_3\text{SiO})(\text{c-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}]_2\}^-$ **2**, $[\text{HNEt}_3]^+\{\text{Ga}[(\text{Me}_3\text{SiO})(\text{c-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}]_2\}^-$ **3a**, and $[\text{C}_{14}\text{H}_{18}\text{N}_2\text{H}]^+[(\text{c-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{GaCl}]^-$ **4** at around 823 K in an air stream. The oxides contained true micropores with very narrow pore size distributions. Some instability of the microporous structures in the presence of water vapor was also demonstrated. The pore structures were not greatly influenced by the group 13 elements and counter cations, but the acidic properties were significantly affected by the silsesquioxane precursors. Aluminum- or gallium-bridged silsesquioxanes, **2**, **3a** and **3b**, are suitable precursors for the production of oxides with large numbers of acidic sites. The strength of the acidic sites can be partly controlled by the selection of group 13 elements and counter cations. The present results confirm that group 13 elements-containing silsesquioxanes are good precursors for novel acidic catalysts. More detailed study on the chemical and structural changes during the calcination of silsesquioxanes, especially on the source of micropores, as well as investigations on their catalytic activities, are now proceeding.

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要 旨

13 族元素含有シルセスキオキサンを前駆体とする多孔質固体酸性酸化物の調製

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新規 13 族元素含有シルセスキオキサン $\text{PhB}[(\text{Me}_3\text{SiO})(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}]$ (**1**) および $[\text{PPN}]^+\{\text{Ga}[(\text{Me}_3\text{SiO})(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}]_2\}^-$ (**3b**) を新たに合成した。さらに, これらの新規シルセスキオキサン, および $[\text{HNEt}_3]^+\{\text{Al}[(\text{Me}_3\text{SiO})(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}]_2\}^-$ (**2**), $[\text{HNEt}_3]^+\{\text{Ga}[(\text{Me}_3\text{SiO})(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}]_2\}^-$ (**3a**), $[\text{C}_{14}\text{H}_{18}\text{N}_2\text{H}]^+\{(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{GaCl}\}^-$ (**4**) 等を 723~923 K で焼成することによって, 約 5.1 Å 径で均一に制御されたマイクロ細孔のみからなり, 330~520 m² g⁻¹ の比表面積を示す多孔質固体酸性酸化物を得た。これらの酸化物の物性の詳細な検討により, 細孔構造が前駆体シルセスキオキサンにほとんど依存しないのに対して, 固体酸性は前駆体分子の構造や含有される 13 族元素, および対

カチオンの影響を大きく受けることを明らかにした。中でもアルミニウムおよびガリウム架橋型シルセスキオキサン **2**, **3a** および **3b** を乾燥空気気流中, 823 K 付近で焼成することによって, 比表面積が大きく, 酸点を豊富に有する酸化物が得られた。特に, **3a** から得られた酸化物は強酸点を有するが, **2** および **3b** を前駆体とした場合には弱~中程度の強度の酸点を豊富に有する酸化物が得られた。しかし, コーナーキャップ型のガリウム含有シルセスキオキサン **4** を前駆体とした場合には, ほとんど固体酸性を示さなかった。酸化物中の 13 族元素の分散性が前駆体分子に依存することを見い出したが, これらが固体酸性の差異の一因として考えられる。

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