Preparation of Microporous Ga–Si–O Materials with Acidic Sites from a Gallium-Bridged Silsesquioxane

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Ga–Si–O materials with acidic sites and uniformly-controlled micropores have been prepared by the calcination of a new gallium-bridged silsesquioxane $[HNEt_3]^+[Ga\{(Me_3Si)(c\text{-}C_5H_9)_7Si_7O_{12}\}_2]^-$.

Group 13 element-containing oxides such as silica–alumina, zeolites and mesoporous silicate-based oxides have been extensively studied because of their great importance in current chemical industries and petroleum refineries, mainly as solid acidic catalysts.[1] On the other hand, heteroatom-containing oligosilsesquioxanes have attracted attention as well-defined, homogeneous models of the active surface sites of the supported catalysts or zeolites.[2] Several silsesquioxanes containing gallium,[3] aluminium,[4] or boron[5] have been synthesized. In addition, some metal-containing silsesquioxanes were found to be convenient precursors for M–Si–O materials with high surface areas and uniformly-controlled micropores.[6] Therefore, acidic oxides with controlled pore structures are expected to be prepared from a certain group 13 element-containing silsesquioxane. Note that the solid acidic catalysts active for 1-butene isomerization have been prepared from a silsesquioxane triol, $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$, deposited on alumina surface followed by calcination in air.[7]

In the present communication, the synthesis of a new gallium-bridged silsesquioxane $[HNEt_3]^+[Ga\{(Me_3Si)(c\text{-}C_5H_9)_7Si_7O_{12}\}_2]^-$ (**1**) and the preparation of Ga–Si–O materials with solid acidity by the calcination of **1** are reported. The pore structures and the acidic characters of the produced oxides are discussed.

A gallium-bridged silsesquioxane **1** was synthesized by the reaction of gallium trichloride (0.5 mmol) with two equivalents of silsesquioxane disilanol **2**[8] (1.0 mmol) in the presence of excess triethylamine (50 mmol) in a benzene–diethyl ether solution at room temperature for 24 h. After separation of triethylammonium chloride by filtration, careful recrystallization by slow diffusion of acetone into a benzene solution afforded colorless microcrystals of **1** in 69% yield.[9] The ^{1}H NMR spectrum clearly shows the presence of two half-caged silsesquioxane cores and one triethylammonium cation in the molecule. The ^{29}Si-NMR spectrum consists of eight peaks of almost the same intensity for sixteen silicon atoms, which indicates the apparent local C_2-symmetry of the siloxane framework of **1**. These spectroscopic results of **1** are in good accordance with the data reported for $[HNEt_3]^+[Al\{(Me_3Si)(c\text{-}C_5H_9)_7Si_7O_{12}\}_2]^-$.[4f] A cyclopentyl derivative of the corner-capped type gallium-containing silsesqui-oxane already reported by Feher et al.,[3] $[C_{14}H_{18}N_2H]^+[(c\text{-}C_5H_9)_7Si_7O_{12}GaCl]^-$ (**3**), was also synthesized for comparison.

The calcination of **1** and **3** in air flow (W/F = 5.0 g h mol^{-1}) for 4 h at 723 K–923 K produced microporous Ga–Si–O materials. The resultant oxide derived from **1** at 823 K is designated as **1**-823. Table 1 summarizes specific surface areas and pore volumes of the produced oxides. The highest BET surface area of 410 m^{2}g^{-1} was achieved by the calcination of **1** at 823 K, whereas the treatment at higher temperature significantly decreased the surface areas. The calcination of **3** at 823 K also produced the oxide with a high surface area of 410 m^{2}g^{-1}.

Figure 1 shows the nitrogen adsorption isotherms of **1**-823 and **3**-823, which are type I characteristic of microporous materials.[10] The inset of Figure 1 shows the pore size distribution of **1**-823 derived from a nitrogen adsorption isotherm by the Saito–Foley method using the sorbent parameters for oxide ions of zeolites.[11] The plot reveals a sharp peak at the pore diameter around 5 Å.

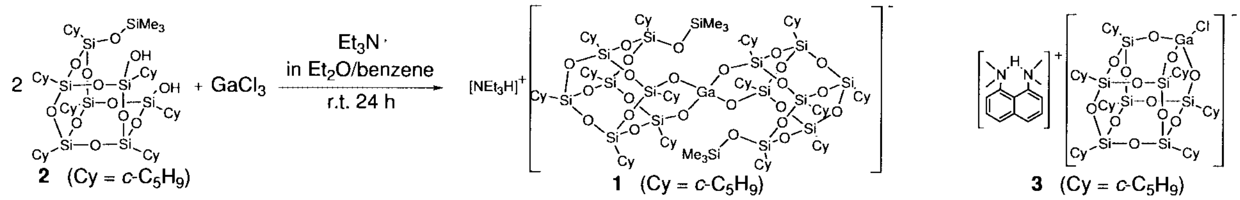
Table 1. Nitrogen sorption data of the oxides prepared by the calcination of **1** or **3** at 723, 823, or 923 K

Sample	BET surface area^b / m^{2}g^{-1}	Pore volume / cm^{3}g^{-1}
1-723	400	0.18
1-823	410	0.20
1-923	330	0.17
3-823	410	0.21
3-923	160	0.08

^{a}All samples were evacuated at 473 K for 2 h. ^{b}Calculated based on the adsorption data of $0.025 < P / P_0 < 0.100$.

In the TG measurement of **1** in air flow, gradual weight loss (57.6%) over the expected decrease by complete oxidation of organic moiety (48.9 %) was observed at 473–823 K. On the other hand, in the case with **3** weight loss started at lower temperature (ca. 400 K), but total mass decrease was very close to the theoretical value. The EDX analyses of **1**-823 showed Si/Ga of 15, slightly lower than that of **1** (Si/Ga = 16). The oxide **3**-823 also showed barely lower Si/Ga ratio (6.7) to that of **3** (7.0). According to the XRD measure-

Scheme 1.



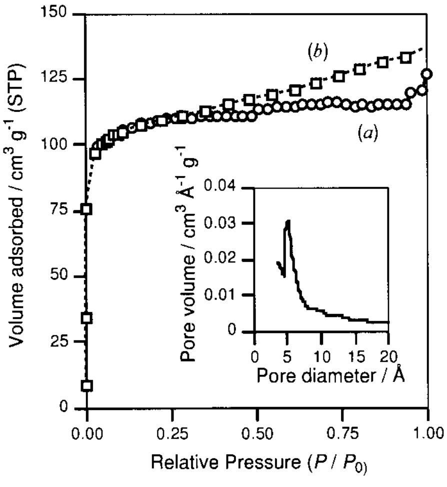


Figure 1. Nitrogen adsorption isotherms of the oxides calcined at 823 K from (*a*) **1** and (*b*) **3**. Inset shows pore size distribution for the **1**-823 material by the Saito-Foley method.

ments, both **1**-823 and **3**-823 were found to be amorphous.

As shown in Figure 2, investigation on the solid acidic characters of **1**-823 and **3**-823 was performed by ammonia TPD. The result for the oxide prepared at 823 K from a silsesquioxane trisilanol, (c-$C_5H_9)_7Si_7O_9(OH)_3$,[2] is also presented for comparison. The TPD spectrum of **1**-823 consists of three broad desorption bands at around 450, 575, and 720 K, indicating the presence of strong acidic sites as well as weak ones. Note that the measurement of HZSM-5 (Si/Al = 20) showed two bands at 450 K and 620 K. Such strong acidic sites have been reported to be predominant in the case with GaMCM-41.[12] The total amount of desorbed ammonia was 0.343 mmol g^{-1}, indicating that about one-third of the gallium atoms included in the oxide are estimated to be responsible for the formation of acidic sites. On the other hand, **3**-823 desorbed a significantly smaller amount of ammonia (less than 0.050 mmol g^{-1}) in spite of its larger content of the gallium species. The EPMA measurement of **3**-823 revealed the formation of large (ca. 10 µm), discrete particles of gallium oxides, whereas the investigation of **1**-823 indicates the absence of such particles of gallium oxides. The relatively low stability of **3** towards high temperature and moisture compared with **1** would be one reason for the lower dispersion of the gallium species, and eventually a smaller amount of acid sites on the surface of **3**-823. Note that preliminary FTIR measurements of pyridine adsorbed on the resulting oxides show a strong band at around 1530 cm^{-1} together with a weak band at 1450 cm^{-1}, clearly indicating the predominant formation of Brönsted acidic sites on their accessible surfaces.[13]

In conclusion, for the first time Ga–Si–O materials with acidic sites were prepared by the calcination of a newly synthesized gallium-bridged silsesquioxane **1** at around 823 K in air stream, whereas the oxides from **3** do not show significant solid acidity. The present results confirm the possibility of gallium-bridged silsesquioxanes such as **1** as good precursors for novel Brönsted acidic catalysts.

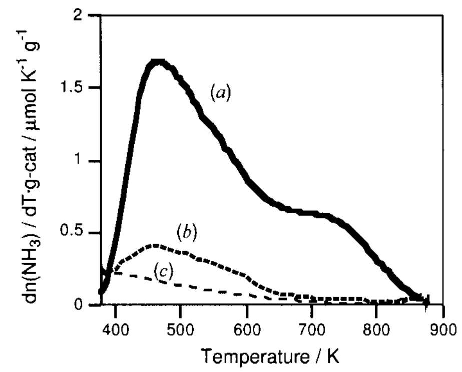


Figure 2. Ammonia TPD of the oxides calcined at 823 K from (*a*) **1**, (*b*) **3** and (*c*) a silsesquioxane trisilanol (c-$C_5H_9)_7Si_7O_9(OH)_3$

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9 Spectroscopic data of **1** ; mp 171.0–172.0 °C; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 9.98 (s, 1H, $[HNEt_3]^+$), 3.21 (br s, 6H, $[HN(CH_2CH_3)_3]^+$), 1.73–1.26 (br m, 112H, CH_2 of Cy (c-C_5H_9)), 1.34 (t, J = 7.1 Hz, 9H, $[HN(CH_2CH_3)_3]^+$), 0.98–0.76 (br m, 14H, *C*H of Cy), 0.11 (s, 18H, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C) δ 45.65 ($[HN(CH_2CH_3)_3]^+$), 28.28, 28.17, 28.04, 27.84, 27.67, 27.52, 27.42, 27.33, 27.20, 27.11, 27.01, 26.95, 26.90, 26.87, 26.79 (CH_2 of Cy), 25.47, 25.20, 24.53, 24.13, 23.78, 22.82, 22.41 (1 : 1 : 1 : 1 : 1 : 1 : 1 : 1 for *C*H of Cy), 8.98 ($[HN(CH_2CH_3)_3]^+$), 2.10 ($Si(CH_3)_3$); $^{29}Si\{^1H\}$ NMR (76 MHz, $CDCl_3$, 0.2 M $Cr(acac)_3$, 25 °C) δ 7.56, −63.28, −63.69, −64.75, −65.15, −65.84, −67.54, −68.00 (1 : 1 : 1 : 1 : 1 : 1 : 1 : 1 : 1). MS (FAB^+) *m/z* 1961 (4) $[M - NEt_3]^+$, 1891 (10) $[M - HNEt_3 - C_5H_9]^+$, 861 (100), 859 (96). Anal. Calcd for $C_{82}H_{160}NO_{24}Si_{16}Ga$ (2063.27): C, 47.74; H, 7.82; N, 0.68%. Found C, 46.74; H, 7.81; N, 0.65%.

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