Preparation of Novel Porous Oxide Catalysts from Metal-Containing Silsesquioxanes

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Several group 4 transition metal- or group 13 element-containing silsesquioxanes with cubic core structures are newly synthesized. The controlled calcination of these metal-containing silsesquioxanes at around 823 K produces porous oxides with high BET surface areas of 330 - 520 m^2g^{-1} and uniformly-controlled micropores of 5 - 6 Å diameter. Metallic oxide species in thes siloxane matrices are well-dispersed. Remarkably, from group 13 elements-containing silsesquioxanes Brönsted acidic oxides are produced. Their acidic properties are greatly affected by the structure of silsesquioxane precursors, and partly controlled by the selection of group 13 elements and counter cations. Differences in the dispersion of oxides of group 13 elements in silica matrixes, which are closely related to the structure of precursors, are considered to be one of the reasons of differences in their acidic characters, while pore textures are not altered by the precursor silsesquioxanes.
Key words: silsesquioxane, titanium, zirconium, aluminum, acidic oxides
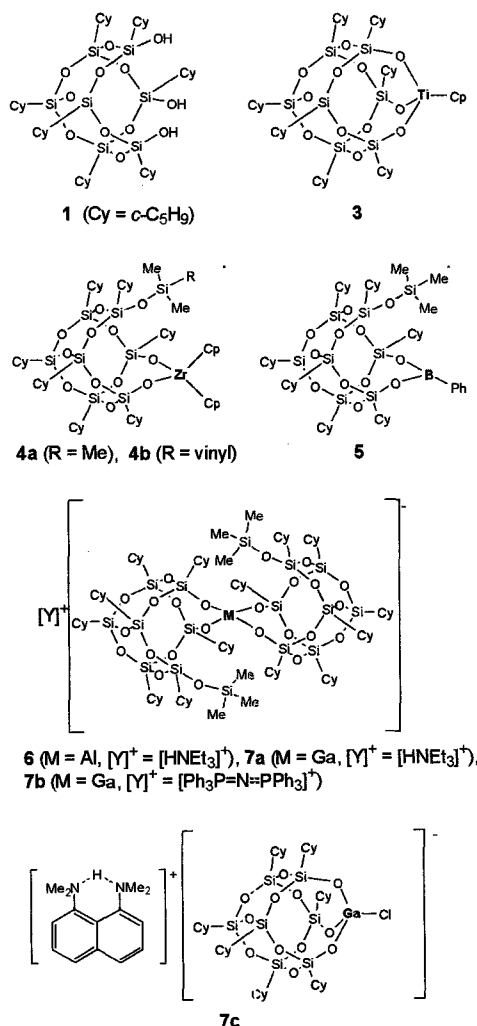
1. INTRODUCTION

Silica-supported metal oxide catalysts play significant roles in the current industrially and commercially important processes.[1] Therefore, development of novel siliceous catalysts with well-defined pore structure and controlled transition metal species is of great significance, whereas precise understanding of the nature of surface active sites and the mechanisms of the reactions proceeded on the surface of heterogeneous catalysts is normally difficult despite of recent marked development in surface spectroscopy.

In this context, metal-containing silsesquioxanes with cubic core structures have attracted much attention from the viewpoint of well-defined, homogeneous models for the active surface sites of the supported catalysts or metal-containing zeolites,[2-7] as well as incompletely condensed oligomers with silanol groups as models for silica supports.[8] Actually, activities of metal-containing silsesquioxanes as *homogeneous* catalysts have been examined.[2-5,7]

In addition to their activities as *homogeneous* catalysts, there are attempts to prepare the *heterogeneous* catalysts from metallasilsesquioxanes.[5,6] We have reported the excellent activities of the oxide catalysts prepared from a silica supported vanadium-containing silsesquioxane for selective photo-assisted oxidation of methane into methanal.[9] Furthermore, we have found for the first time that a titanium-containing silsesquoxane is a convenient precursor for Ti-Si-O materials with high surface areas and uniformly-controlled micropores.[10] Afterwards, the preparation of microporous oxides from chromium-containing silsesquioxanes and their catalytic activities were reported by other research groups.[11]

In the present proceeding, our recent attempts of the synthesis of several new group 4 transition metal- or

Scheme I

1 (Cy = *c*-C5H9)   3

4a (R = Me), 4b (R = vinyl)   5

6 (M = Al, [Y]+ = [HNEt3]+), 7a (M = Ga, [Y]+ = [HNEt3]+),
7b (M = Ga, [Y]+ = [Ph3P=N=PPh3]+)

7c

group 13 element-containing silsesquioxanes and the preparation of microporous oxides by the controlled calcinations of them are reported.[10,12-14] Characterization of the resulting oxides by means of spectroscopic analyses is discussed. Remarkably, solid acidic characters of the oxides prepared from group 13 element-containing silsesquioxanes are investigated in detail.

2. EXPERIMENTAL

A silsesquioxane trisilanol 1,3,5,7,9,11,14-hepta-cyclopentyltricyclo[7.3.3.1^{5,11}]heptasiloxane*endo*-3,7,14 -triol (1) were purchased from Aldrich and used as received. Organic solvents and amines were purchased from Nacarai Tesque Co. Ltd. and carefully distilled using appropriate drying reagents just before use. The detailed synthetic procedures of $CpTi[(c-C_5H_9)_7Si_7O_{12}]$ (Cp = cyclopentadienyl, 3),[10] $Cp_2Zr[(c-C_5H_9)_7Si_7O_{11}-OSiMe_2R]$ (R = Me (4a), vinyl (4b)),[12] $PhB[(c-C_5H_9)_7Si_7O_{11}OSiMe_3]$ (5),[14] $[Y]^+[\{(c-C_5H_9)_7-Si_7O_{11}(OSiMe_3)\}_2Ga]^-$ ($[Y]^+$ = $[HNEt_3]^+$ (7a),[13] $[Ph_3P=N=PPh_3]^+$ (7b)[14]) have been reported elsewhere. $[HNEt_3]^+[\{(c-C_5H_9)_7Si_7O_{11}(OSiMe_3)\}_2Al]^-$ (6)[15], $[C_{14}H_{18}N_2H]^+[(c-C_5H_9)_7Si_7O_{12}GaCl]^-$ (7c)[16] and silsesquioxane disilanols $(c-C_5H_9)_7Si_7O_9-(OSiMe_2R)(OH)_2$ (R = Me (2a),[17] vinyl (2b)[12]) were also prepared according to known literature procedures.

Calcination of silsesquioxanes (typically 0.50 g) was performed in a stream of dried, CO_2-free air (W/F = 5.0 g h mol^{-1}) by using a fixed-bed flow-type quartz reactor (i.d. 8.0 mm) under atmospheric pressure. Temperature was raised by 10 K min^{-1} and held at the prescribed level for 4 h. The resulting oxides were analyzed by nitrogen gas adsorption, XRD, DRIFTS, XPS, SEM, EPMA, ammonia TPD and so on.

3. RESULTS AND DISCUSSION

3.1 Synthesis of New Ti- or Zr-Containing Silsesquioxanes

$CpTi[(c-C_5H_9)_7Si_7O_{12}]$ (3),[10] a cyclopentyl analogue of known titanium-containing silsesquioxane,[18] was prepared by the reaction of $CpTiCl_3$ and a silsesquioxane trisilanol (1, yield 43%). The reaction of zirconocene dichloride with silsesquioxane disilanols (2a, 2b) in the presence of excess amine produces $Cp_2Zr[(c-C_5H_9)_7Si_7O_{11}OSiMe_2R]$ (R = Me (4a, 87%), vinyl (4b, 83%)) in high yields.[12] Scheme I shows their structures, which have been deduced on the basis of ^1H, ^{13}C, ^{29}Si NMR, FAB-MASS, and for 4a preliminary single crystal X-ray diffraction study.[12]

3.2 Preparation of Microporous Oxides from Ti- or Zr-Containing Silsesquioxanes

The controlled calcination of 3 and 4b in a stream of air at around 823 K yields porous mixed oxides.[10,12] Similarly, calcination of an incompletely-condensed silsesquioxane 1 also produces porous silica. The resultant oxides are further designated as 3-723 (suffix number is the calcination temperature in K). The XRD analysis shows their amorphous nature. Table I shows BET surface areas of the oxides. Note that the calcination of them at below 623 K only yields black nonporous materials. The mostly suitable treatment temperature is 823 K to produce oxides with surface

Table I. BET surface areas of group 4 metal-containing oxides

Oxides[a]	BET surface area (m^2g^{-1})
1-823	420
3-723	160
3-823	360
3-923	280
4b-823	370

a) All samples were evacuated at 473 K for 2 h just before the measurement. Numbers represent the calcination temperature (K)
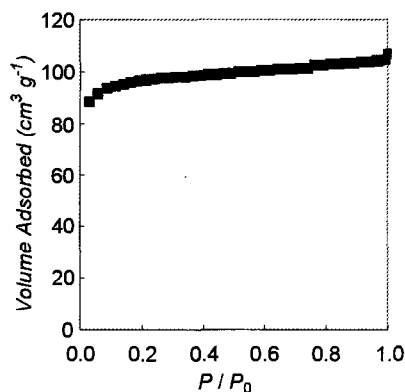

Figure I. Nitrogen adsorption isotherm of 4b-823 at 77 K. the sample was pretreated at 573 K under vacuum for 2 h

areas of 360 - 420 m^{2}g^{-1}, whereas at higher temperature their specific surface areas greatly decrease.

Figure 1 shows the nitrogen adsorption isotherm of 4b-823. Note that all the oxides prepared by the calcinations of 1, 3, and 4b at above 823 K show similar "type-I" isotherms, diagnostic of microporous materials.[19] The analysis of isotherms by MP method revealed that their pore size distribution of these oxides is very narrow (at around 5 – 6 Å).

The XPS (X-ray photoelectron spectroscopic) study of 3-823 revealed that the ratio of Ti / Si was 0.088, in spite of the EDX analysis which showed Ti / Si of 0.14 in good agreement with the composition of 3. On the other hand, the Ti 2p$_{3/2}$ peak was separated into two peaks, one centered at 460.1 eV and the other at 458.5 eV (the ratio of the peak areas = 0.82 : 0.18). For titanosilicates, the former and latter peaks have been assigned to a framework Ti and an extraframework Ti phase, respectively.[20] These results are consistent with an idea of the formation of cluster-like Ti oxide species isolated in the siloxane matrices.[21] Other spectroscopic results also support this idea.

3.3 Synthesis of New Group 13 Element-Containing Silsesquioxanes

Several new group 13 element-containing oligosilsesquioxanes, as well as already known ones, were prepared.[13,14] The reaction of dichlorophenylborane with a silsesquioxane disilanol 2a in the presence of excess triethylamine afforded a boron-containing silsesquioxane 5 in the yield of 70% (Scheme I). The NMR analysis of 5 is consistent with the local C_s symmetry of its siloxane framework. In addition, there was no sign of the coordination of amines or solvents by

^{1}H NMR. A gallium-bridged silsesquioxane **7a** was obtained in 69% yield by the reaction of gallium trichloride with two equivalents of **2a** in the presence of excess triethylamine at room temperature. In order to investigate the effects of the counter cation on the nature of the resulting oxides, a PPN (bis(triphenylphosphoranylidene)ammonium) salt **7b** was prepared by the cation exchange of **7a** with PPNCl. The ^{1}H NMR spectra of **7a** and **7b** clearly show the presence of two half-cage silsesquioxane cores and one cation in each molecule. The ^{29}Si-NMR spectra indicate the apparent local C_2-symmetry of the siloxane framework of each molecules. In addition, $[C_{14}H_{18}N_2H]^+[(c\text{-}C_5H_9)_7Si_7O_{12}GaCl]^-$ (**7c**)^{16} and an aluminum-bridged silsesquioxane **6**^{15} were also prepared for comparison.

Table II. BET surface areas of group 13 element-containing oxides

Oxides$^{a)}$	BET surface area (m^2g^{-1})	Total pore volume (cm^3g^{-1})
5-823	330	0.11
6-723	520	0.23
6-823	460	0.20
6-923	360	0.16
7a-723	400	0.18
7a-823	410	0.20
7a-923	330	0.17
7b-823	410	0.20
7c-823	410	0.21

a) All samples were evacuated at 473 K for 2 h just before the measurement. Numbers represent the calcination temperature (K)

3.4 Preparation of Acidic Microporous Oxides from Group 13 Element-Containing Silsesquioxanes

Group 13 element-containing silsesquioxanes were further subjected to the calcinations in air to produce amorphous oxides.^{13,14} Again the mostly suitable temperature is 823 K (see Table II). At lower temperatures, 723 – 773 K, severe deposition of carbonaceous materials was observed, although larger specific surface areas were achieved. Figures 2 and 3 show nitrogen adsorption isotherms and pore size distributions estimated by Saito-Foley method.^{22} As can be seen in Figure 3, these oxides are found to possess uniformly-controlled micropores of 5 - 6 Å diameter, indicating that differences in the structures and metallic
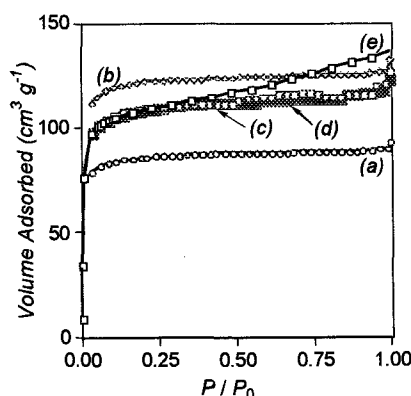
species do not effect much on the pore textures of the oxides. Note that isotherm of **7b-823** completely coincides with that of **7a-823**, indicating lack of influence of the bulky cationic species (PPN$^+$ versus HNEt$_3^+$). This is probably due to the complete loss of the HNEt$_3^+$ or PPN$^+$ cation during the heat-up before the formation of micropores started by the combustion of cyclopentyl groups. The thermogravimetric analyses of **7a** and **7b** support this idea.

Remarkably, from group 13 element-containing silsesquioxanes Brönsted acidic oxides are produced. Their acidic properties were measured by ammonia TPD (temperature programmed desorption) analysis as shown in Figure 4. The result of **1-823** is also presented for comparison. The TPD spectrum of **5-823** shows that only a small amount of weak acidic sites exist on the surface of this oxide. The TPD spectra of **7a-823** consists of three broad desorption bands at around 450, 575, and 720 K, indicating the lack of uniformity of gallium species presented on the surface of this oxide. This **7a-823** desorbed a large amount of ammonia (0.343 mmol g^{-1}). The band at 720 K, however, is not observed in the case of **7b-823**, indicating significant effects of counter cations on the acidic properties of the oxides. On the other side, **7c-823** prepared from a silsesquioxane including tripodal gallium species has only very small amount of acidic sites. Amorphous aluminosilicate **6-823** has acidic sites of moderate strength. This sample desorbed 0.289 mmol g^{-1} of ammonia, corresponding to about one-third of the amount of aluminum included in the oxide. Note that the investigation by FTIR of pyridine adsorbed on the gallium-containing oxides, **7a-823**, distinctly indicates the predominant formation of Brönsted acidic sites on the accessible surface. This is in contrast to the results reported by Maxim et al., in which the calcinations of an aluminosilsesquioxane bearing a proton produced Lewis acidic oxides.^{23}

According to the XPS study the surface Si / M (M = B, Al, Ga) atomic ratios of **5-823**, **6-823**, and **7b-823** are very close to their bulk Si / M atomic ratios. The surface Si / Ga ratio of **7a-823** is, however, significantly high (28). This suggests the formation of segregated gallium species in **7a-823**,^{21} while atomically dispersed gallium species are considered to be formed in **7b-823**. These results indicate that differences of counter cation significantly influence the dispersion of Ga species on the surface of the resulting oxides. This idea is also consistent with the TPD study (see above).
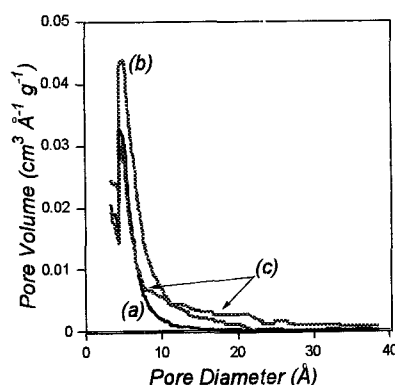
Figure 2. Nitrogen adsorption isotherms of (a) **5-823**, (b) **6-823**,(c) **7a-823**, (d) **7b-823**, and (e) **7c-823**. The sample was pretreated at 573 K under vacuum for 2 h

Figure 3. Pore size distributions estimated by Saito-Foley method. (a) **5-823**, (b) **6-823**, and (c) **7a-823**.

4. EPILOGUE

Several group 4 transition metal- and group 13 element-containing silsesquioxanes were newly synthesized and unambiguously characterized. The controlled calcination of these metal-containing silsesquioxanes at around 823 K produces porous amorphous oxides with high BET surface areas of 330 - 520 m^2g^{-1} and uniformly-controlled micropores of 5 - 6 Å diameter. While surface area is affected by precursor molecules, pore textures are not altered by changing metallic species and/or counter cations. From group 13 elements-containing silsesquioxanes Brönsted acidic oxides are produced. Their acidic properties are greatly affected by the structure of silsesquioxane precursors, and partly controlled by the selection of group 13 elements and counter cations. Differences in the dispersion of oxides of group 13 elements in silica matrices, which are closely related to the structure of precursors, are considered to be one of the reasons of differences in their acidic characters. Among them, oxides prepared by the calcination of aluminium-containing silsesquioxanes show excellent solid acidity.

The present results indicate the possibility of metallasilsesquioxanes as excellent precursors for porous oxide catalysts. The investigation on their catalytic activities will be reported in due course.

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Figure 4. Ammonia TPD spectra of (a) **5**-823, (b) **6**-823, (c) **7a**-823, (d) **7b**-823, (e) **7c**-823, and (f) **1**-823.

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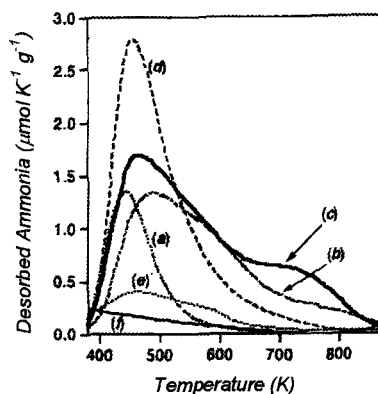[23] N. Maxim, P. C. M. M. Magusin, P. J. Kooyman, J. H. M. C. van Wolput, R. A. van Santen, H. C. L. Abbenhuis, *Chem. Mater.*, **13**, 2958-2964 (2001).