

Synthesis of Microporous Ti-Si-O Materials from a Titanium-containing Oligosilsesquioxane

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Microporous Ti-Si mixed oxides with high surface areas were prepared by the calcination of a titanium-containing oligosilsesquioxane with a cubic core structure, $[\text{CpTi}(\text{R}_7\text{Si}_7\text{O}_{12})]$ ($\text{R} = \text{c-C}_5\text{H}_9$) **1b**, or silica-supported **1b**.

Oligometallasilsesquioxanes such as a compound **1a** have attracted attention from the view point of well-defined, homogeneous models for the active surface sites of the supported catalysts or metal-containing zeolites.¹ Recently, the catalytic activities of titanium-containing oligosilsesquioxanes²⁻⁵ including **1a**³ or **1a** immobilized in MCM-41⁵ for epoxidation of olefins have been reported from the viewpoint of soluble analog of titanosilicates, such as TS-1, of remarkable catalytic properties.⁶

On the other hand, in order to investigate the functions of oligometallasilsesquioxanes both as homogeneous models of supported catalysts and as precursors for porous oxide catalysts, we have recently prepared a cyclopentyl derivative of vanadium-containing silsesquioxane, and reported its excellent catalytic activity towards the photooxidation of hydrocarbons.^{7,8} Furthermore, we have found that the oxide catalysts prepared by the calcination of silica-supported vanadium-containing oligosilsesquioxane showed excellent activities towards the selective photo-assisted catalytic oxidation of methane into methanol.⁹ The resultant oxide catalysts possessed markedly larger specific surface areas than those of the parent silica supports, and were rich in both micropores and mesopores. Note that there were reports on the synthesis of microporous ceramics from polymeric precursors including siloxane cage structures.¹⁰

In the present communication, we report the preparation of a titanium-containing silsesquioxane **1b**, a new cyclopentyl derivative of **1a**. In addition, we found that the calcination of **1b** itself produced microporous Ti-Si-O materials of high surface areas and relatively uniform pore size distributions. The loading of **1b** onto the silica-support followed by the calcination significantly increased its surface area.

Preparation of a titanium-containing oligosilsesquioxane **1b** was carried out as described in the literature for **1a**.¹¹ The reaction of cyclopentadienyltitanium trichloride with incompletely-condensed silsesquioxane **2b**, which was prepared by the hydrolytic condensation of cyclopentyltrichlorosilane, gave white microcrystals of **1b** in 43% yield.¹² The calcination of **1b** was performed in air flow for 4 h at 723 K \sim 823 K, and the resultant oxides are further designated as TOS-723 (suffix number is the calcination temperature in K). No significant sublimation of **1b** was observed during the calcination, although some oligo-organosilsesquioxanes were reported to be extremely volatile.¹³

The calcination of **1b** produced microporous mixed oxides. Table 1 summarizes specific surface areas of the oxides, indicating that the calcination temperature was critical. TOS-823 showed high BET surface area of 359 m^2g^{-1} , whereas that of TOS-723 was only 158 m^2g^{-1} . The adsorption isotherms of TOS-823 were Type I characteristic of microporous materials

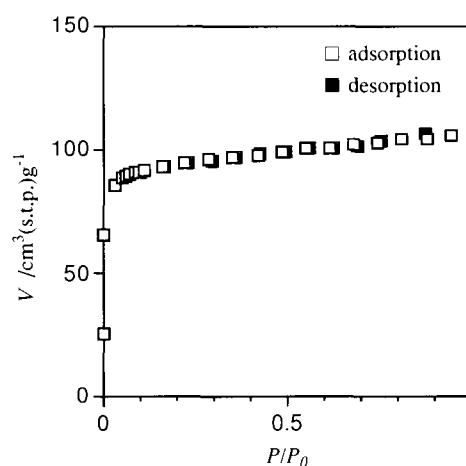
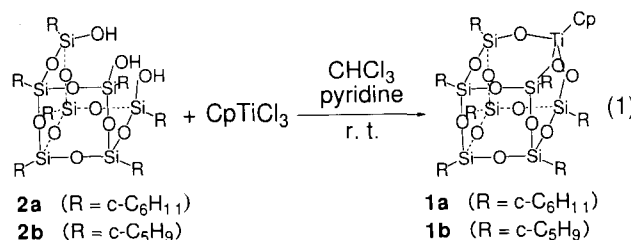


Figure 1. N_2 adsorption/desorption isotherms of TOS-823 at 77 K. The sample was pretreated at 473 K in vacuum for 2 h.

Table 1. Specific surface areas of TOS and TOS/silica samples^a

samples	BET surface area ^b / m^2g^{-1}
TOS-723	158 [187]
TOS-823	359 [406]
silica (Wako 60)	626
TOS/silica-723	703
TOS/silica-823	780

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

^b The figures in square brackets are Langmuir surface areas.

(Figure 1).¹³ On the other hand, TOS-723 afforded a Type II curve associated with a steep increase in the adsorption amount at low p/p_0 , indicating the presence of both micro- and mesopores. Pore-size distribution of TOS-823 estimated by the MP method is shown in Figure 2(a). The plot reveals a sharp peak at 0.35 nm. However, pore radius calculated by the MP method were not quantitatively reliable in this case, because they greatly affected by

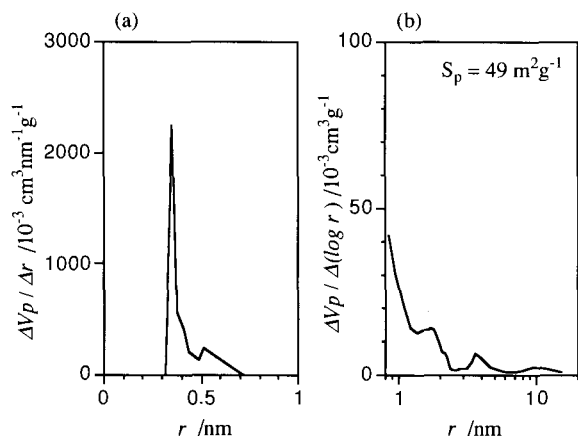


Figure 2. Pore-size distributions of TOS-823 (a) by the MP method calculated from the adsorption isotherm, and (b) by the Dollimore-Heal method using the desorption data.

the selection of standard isotherms. Figure 2 (b) shows the pore-size distribution in the mesopore range derived from the desorption isotherm on using the Dollimore-Heal method. There were very small amount of mesopores, consistent with the results shown in Figure 1 and 2(a). It should be noted that silica prepared by the calcination of an incompletely-condensed silsesquioxane **2b** at 823 K also afforded type I isotherms and was proved to have a large BET surface area ($391 \text{ m}^2 \text{ g}^{-1}$).

There were no peaks in the range $3^\circ < 2\theta < 70^\circ$ in the XRD patterns of both TOS samples, indicating these oxides were amorphous. According to XPS study, the surface of TOS-823 was composed of 27.4 atom% of Si, 2.4 atom% of Ti, and 62.1 atom% of O, together with 8.1 atom% of both carbide and graphitic carbon. The ratio of Ti / Si was 0.088. On the other hand, the EDX analysis showed Ti / Si of 0.14, in good agreement with the composition of **1b**. 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 a extraframework Ti phase, respectively.¹⁴ Further spectroscopic investigations on the state of titanium are now in progress.

In order to examine the possibility of the construction of nanostructure on the wall of meso- or macroporous materials by the 'post-synthesis' using oligometallasilsesquioxanes, we conducted the synthesis of mixed oxides from silica-supported **1b**. The supported molecules were prepared by incipient wetness impregnation from pentane solution of **1b** using silica (Wako 60, evacuated at 423 K for 2 h, weight ratio **1b** : silica = 2 : 5, Ti 2.0 mol%). The calcination of them in air flow for 4 h produced the mixed oxides, designated as TOS/silica-823.

Table 1 also shows surface areas of TOS/silica samples. These samples were found to possess significantly larger surface areas than the silica support. It should be noted that TOS/silica

samples adsorbed larger amounts of nitrogen at low p/p_0 than the parent support, indicating the formation of micropores. On the other hand, the Dollimore-Heal plots indicated that there were no significant changes in their structures of $r > 2 \text{ nm}$ by the loading of **1b** followed by the calcination. Since simple sum of the data of silica support and TOS samples can not account for the increases in surface areas, interaction between the silica surface and **1b** during the heat treatment seems to play an important role.

In conclusion, we prepared amorphous Ti-Si mixed oxides with high surface areas and well-defined micropores by the calcination of a titanium-containing oligosilsesquioxane **1b**. The TOS/silica materials prepared from the silica-supported **1b** possessed larger surface areas than that of the support. The present results indicate the possibility of oligometallasilsesquioxanes as excellent precursors for porous oxide catalysts. We are now investigating their catalytic properties, especially the shape selectivities.

References and Notes

- a) J. F. Brown Jr. and L. H. Vogt, *J. Am. Chem. Soc.*, **87**, 4313 (1965). b) F. J. Feher and T. A. Budzichowski, *Polyhedron*, **14**, 3239 (1995). c) R. H. Baney, M. Itoh, A. Sakakibara, and T. Suzuki, *Chem. Rev.*, **95**, 1409 (1995). d) R. Murugavel, A. Voigt, M. G. Walawalker, and H. W. Roesky, *Chem. Rev.*, **26**, 2205 (1996). e) P. Harrison, *J. Organomet. Chem.*, **542**, 141 (1997). f) F. J. Feher, T. A. Budzichowski, K. Rahimian, and J. W. Ziller, *J. Am. Chem. Soc.*, **114**, 3859 (1992).
- a) M. Crocker and R. H. M. Herold, Pat. Appl., PCT/EP96/05873. b) M. Crocker, R. H. M. Herold, and A. G. Orpen, *Chem. Commun.*, **1998**, 2411.
- H. C. L. Abbenhuis, S. Krijnen, and R. van Santen, *Chem. Commun.*, **1997**, 331.
- T. Maschmeyer, M. C. Klunduk, C. M. Martin, D. S. Shephard, J. M. Thomas, and B. F. G. Johnson, *Chem. Commun.*, **1997**, 331.
- S. Krijnen, H. C. L. Abbenhuis, R. W. J. M. Hanssen, J. H. C. van Hooff, and R. van Santen, *Angew. Chem., Int. Ed. Engl.*, **37**, 356 (1998).
- I. W. C. E. Arends, R. A. Sheldon, M. Wallau, and U. Schuchardt, *Angew. Chem., Int. Ed. Engl.*, **36**, 1144 (1997), and references therein.
- K. Wada, M. Nakashita, A. Yamamoto, H. Wada, and T. Mitsudo, *Chem. Lett.*, **1997**, 1209.
- K. Wada, M. Nakashita, A. Yamamoto, H. Wada, and T. Mitsudo, *Res. Chem. Intermed.*, in press.
- K. Wada, M. Nakashita, A. Yamamoto, and T. Mitsudo, *Chem. Commun.*, **1998**, 133.
- P. A. Agaskar, *J. Chem. Soc., Chem. Commun.*, **1992**, 1024.
- I. E. Buys, T. W. Hambley, D. J. Houlton, T. Maschmeyer, A. F. Masters, and A. K. Smith, *J. Mol. Catal.*, **86**, 309 (1994).
- Synthesis of a titanium-containing silsesquioxane, **1b**. Cyclopentadienyltitanium trichloride (0.357 g, 1.63 mmol) in CHCl_3 (30 cm^3) was added at room temperature to a stirred CHCl_3 solution (30 cm^3) of **2b** (1.51 g, 1.72 mmol). A resulted pale yellow solution was decolorized immediately by the addition of pyridine (6 cm^3). The solvent was then evaporated at room temperature to leave an off-white yellow solid. This was extracted with hexane (60 cm^3) to give a pale yellow filtrate and a white residue of $\text{C}_5\text{H}_6\text{NCl}$. The filtrate was evaporated, and the product was obtained by recrystallization from a CHCl_3 solution. Yield 43 %. ^1H NMR (400 MHz, CDCl_3) δ 6.46 (s, 5H), 1.72-0.93 (br m's, 63 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 115.90 (C_5H_5), 27.64, 27.44, 27.31, 27.09, 27.04 (CH_2), 22.43, 22.34 (3 : 4 for CH).
- S. J. Greg and K. S. W. Sing, "Adsorption, Surface Area and Polarity," 2nd ed., Academic Press, London (1982).
- T. Blasco, M. A. Camblor, J. L. G. Fierro, and J. Perez-Pariente, *Microporous Mater.*, **3**, 259 (1994).