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Ti-bridged silsesquioxanes as precursors of silica-supported titanium oxide catalysts for the epoxidation of cyclooctene

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ABSTRACT

Silica-supported titanium oxide catalysts were prepared by the controlled calcination of Ti-bridged polyhedral oligomeric silsesquioxanes (POSS) bearing four Si–O–Ti bonds, $Ti[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMe_2R)]_2$ (**1a**; R = vinyl, **1b**; R = methyl) and $Ti[(c\text{-}C_5H_9)_8Si_8O_{13})]_2$ (**2**), supported on various silicas, and these catalysts showed excellent activities for the epoxidation of cyclooctene by ^{t}BuOOH as an oxidant to selectively give cyclooctene oxide in high yields. On the other hand, catalysts prepared using a corner-capped-type Ti-containing POSS, $CpTi[(c\text{-}C_5H_9)_7Si_7O_{12}]$ (**3**, Cp = cyclopentadienyl), or tetraisopropoxytitanium (**4**) showed lower activities. The catalysts prepared from Ti-bridged POSS can be easily separated from the reaction mixture and reused without a significant loss of activity. These catalysts were also applicable for the epoxidation of limonene. A spectroscopic study revealed that calcination of Ti-bridged POSS supported on silica gave isolated tetrahedral Ti(IV) species, which would be responsible for the high activity, while calcination of silica-supported **3** or **4** gave aggregated surface titanium oxide species.

1. Introduction

Siliceous group 4 transition metal catalysts, such as Ti-containing zeolites, are widely used in current chemical industries [1–3]. In particular, titanosilicates such as TS-1 generally show activity that is superior to that of amorphous TiO_2–SiO_2 in the epoxidation of small alkenes [3–5]. However, titanium-containing zeolites generally have steric limitations regarding applicable substrates because of their microporous nature. Therefore, the development of novel titanium catalysts with suitable meso- and/or macropores, which contain well-dispersed titanium species, is of great significance.

On the other hand, metal-containing POSS (polyhedral oligomeric silsesquioxanes) have attracted attention as well-defined, homogeneous models of solid siliceous catalysts [6–15]. In particular, the catalytic activities of Ti-containing POSS for the epoxidation of alkenes have been examined [16–23]. In addition to their activities as homogeneous catalysts, their application to heterogeneous catalysis using metal-containing POSS as precursors has been examined [10,13,15,24–31]. The preparation of microporous silicas containing well-dispersed metal oxide species by the controlled calcination of metal-containing POSS has been reported [32–42]. Furthermore, the authors have prepared catalysts possessing both mesopores and micropores by the impregnation of metallic salts and POSS ligands onto suitable supports followed by calcination, and these catalysts showed excellent activities for both the aerobic oxidation of benzylic alcohols in water [43] and the hydroformylation of alkenes [44]. In this context, we could expect that it would be easier to prepare silica-supported monomeric Ti(IV) catalysts using Ti-bridged POSS in place of usual Ti-containing precursors such as $Ti(O^iPr)_4$ [45].

We report here the preparation of silica-supported titanium oxide catalysts using Ti-containing POSS as precursors. These oxide catalysts showed excellent activities for the epoxidation of cyclooctene by ^{t}BuOOH. The effects of various titanium sources on the activities and physical properties of the thus-prepared oxide catalysts by calcination were examined to identify suitable structures for the required titanium precursors. Changes in the state of Ti-containing POSS during calcination were also investigated.

2. Experimental

2.1. Materials and methods

Ti-containing POSS were prepared and subsequent manipulations were performed under an argon atmosphere using standard Schlenk techniques. Dehydrated toluene (Wako) was used as received. Cyclooctene (Nacalai Tesque), limonene (Wako), ^{t}BuOOH in a decane solution (5.5 M, Fluka), tetrakis(dimethylamido)titanium (Gelest), tetraisopropoxytitanium (**4**; Nacalai Tesque), $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ (Aldrich), and $(c\text{-}C_5H_9)_8Si_8O_{11}(OH)_2$ (Aldrich) were obtained commercially and used without further purification. A platinum catalyst (Karsted's catalyst, (divinyltetramethyldisiloxane)platinum(0) (2.1–2.4 wt.%) in xylene) was obtained from Gelest. $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2(OSiMe_2R)$ (R = vinyl [26], methyl [46]),

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$Ti[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMe_2R)]_2$ (**1a**; R = vinyl [26], **1b**; R = methyl [18,26]), and $CpTi[(c\text{-}C_5H_9)_7Si_7O_{12}]$ (**3**) [33] were synthesized based on methods described in previous reports. Dimethylsiloxy-functionalized silica ($SiMe_2$(H)-silica, Aldrich) and Cabosil (HS-5, Cabot) were used as received. Mesoporous MCM-41 was prepared based on the method in the literature [47]. JRC silicas were obtained from the Catalysis Society of Japan. The BET surface areas of JRC-SIO-1, -5, -6, -7, and -8 were 104, 174, 103, 88, and 316 $m^2\,g^{-1}$, respectively.

2.2. Synthesis of $Ti[(c\text{-}C_5H_9)_8Si_8O_{13})]_2$ (2)

To a solution of $(c\text{-}C_5H_9)_8Si_8O_{11}(OH)_2$ (1481 mg, 1.5 mmol) in anhydrous toluene (25 cm^3), tetrakis(dimethylamido)titanium (168 mg, 0.85 mmol) in anhydrous toluene (20 cm^3) was dropwise added, and the mixture was stirred at room temperature overnight. After the solvent was evaporated, the resulting off-white solid was extracted with hexane (35 cm^3). Filtration using a 0.45-μm PTFE filter gave a clear solution. After the evaporation of hexane, **2** was obtained by recrystallization by slow diffusion of acetonitrile into a toluene solution. Yield 89%. M.p. 260 °C (decomp.). ^1H NMR (400 MHz, C_6D_6, 25 °C) δ 1.94–1.55 (128 H, br m), 1.22–1.14 (16 H, br m); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C) δ 27.81, 27.76, 27.73, 27.59, 27.36, 27.35, 27.31 (CH_2 of Cy), 23.39, 23.02, 22.49 (1: 2: 1, CH of Cy); $^{29}Si\{^1H\}$ NMR (76 MHz, C_6D_6, 0.02 M $Cr(acac)_3$, 25 °C) δ −64.83, −67.65, −68.22 (1: 2: 1). Anal. Calcd for $C_{80}H_{144}O_{26}Si_{16}Ti$ (2019.22): C, 47.59; H, 7.19. Found C, 47.32; H, 6.93.

2.3. Physical and analytical measurements

Solution-phase NMR spectra were recorded on JEOL JNM-EX-400 instruments. ^1H and ^{13}C spectra were referenced to internal solvent resonances and reported relative to $SiMe_4$. Chemical shifts for the ^{29}Si nuclei were referenced to an external $SiMe_4$ resonance. Elemental analyses were performed at the Microanalytical Center of Kyoto University. The TG-TDA study was performed using a RIGAKU TG8120 system. The sample (*ca.* 5 mg) was heated at a rate of 10 °C min^{-1} under a stream of air (50 $cm^3 min^{-1}$). Diffuse reflectance infrared Fourier transform (DRIFT) spectra were recorded using a Nicolet Magna-IR 560 FT-IR spectrometer. An uncalcined sample (*ca.* 10 wt.%, diluted with KBr powder) was heated in air at an approximate rate of 10 °C min^{-1}, and the spectrum was recorded after the sample was held at the prescribed temperature for 10 min. X-ray fluorescence (XRF) analysis was performed using a Spectro XEPOS-MS II (25 W).

The oxide catalysts were analyzed by nitrogen gas adsorption, XRD, XPS, and UV–Vis spectroscopy. Nitrogen adsorption/desorption isotherms were obtained with a computer-controlled automatic gas sorption system (Quantachrome NOVA 4200e). Samples were degassed at 573 K for 30 min just before the measurements. The mean pore diameter was calculated from the pore volume and the specific surface area assuming that the pore was cylindrical. X-ray powder diffraction patterns were recorded using Cu Kα radiation (30 kV, 30 mA) and a carbon monochromator (XRD: XD-D1, Shimadzu). X-ray photoelectron spectra (XPS) 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 Torr; 133.3 N m^{-2}). The spectra were measured at room temperature using Mg Kα radiation (1254 eV) generated by an X-ray tube operating at 15 kV, 400 W. The electron take-off angle was set at 45°. Binding energies were referenced to the C 1s level of residual graphitic carbon [48]. UV–Vis diffuse reflectance spectra were measured with a JASCO V-650 spectrophotometer, in which reflected beams were gathered by an integrating sphere (50 mm inner diameter). A UV cell (10 mm × 40 mm, inner thickness 1.0 mm) equipped with a branched chamber and a stop valve was used to avoid any contact with moisture. The catalyst submitted for measurement was heated in the branched chamber at 473 K under atmospheric pressure for 30 min and evacuated at 673 K followed by treatment under 100 Torr of oxygen at 673 K for 1 h. The catalyst was then transferred to the UV cell, and spectra were taken *in vacuo*. Barium sulfate (Nacalai Tesque) was used as a background. All of the spectra were modified in terms of the Kubelka–Munk function. Leaching of titanium species from the catalysts during the reaction was investigated by an ICP atomic emission spectroscopic analysis using a Shimadzu ICPS-1000III analyzer.

2.4. Preparation of an oxide catalyst from silica-tethered Ti-POSS

$SiMe_2$(H)-functionalized silica gel ($SiMe_2$(H)-silica, 1.0 g) was treated with a toluene solution (30 cm^3) of a Ti-bridged POSS (**1a**) (103 mg, 0.052 mmol) in the presence of Karsted's catalyst (0.0022 mmol, 0.040 cm^3) under an Ar atmosphere. The mixture was stirred at 45 °C for 24 h. Elemental analysis of the support (C 3.83%, H 1.37%) indicated the presence of *ca.* 3.2 $SiMe_2$(H) groups in a unit surface area of 1 nm^2. After filtration, washing of the resulting solid three times with toluene in air and subsequent vacuum-drying gave a tethered catalyst that was designated as **1a**-$SiMe_2$(H)-silica. There was no sign of **1a** in the filtrate and washing solutions after hydrosilylative condensation, indicating that all of **1a** was successfully tethered onto silica. The calcination of **1a**-$SiMe_2$(H)-silica in air at 550 °C for 2 h afforded an oxide catalyst, **1a**-$SiMe_2$(H)-silica-cal.

2.5. Preparation of oxide catalysts from silica-supported Ti-POSS

A typical preparation procedure of the silica-supported titanium oxide catalyst using Ti-POSS is as follows: $SiMe_2$(H)-silica (1.0 g) was impregnated with a toluene solution (3.0 cm^3) of **1a** (98 mg, 0.050 mmol) at 60 °C in air (however, the impregnation of **4** was performed in an Ar atmosphere to avoid the hydrolysis of **4** caused by adventitious contact with moisture). Calcination of the resulting powder (powder derived from **4**, as well) in air at 550 °C for 2 h afforded an oxide catalyst (Si/Ti molar ratio; 350) that was designated as **1a**@$SiMe_2$(H)-silica-cal.

2.6. Catalytic epoxidation of cyclooctene

All of the reactions were performed with the use of hot stirrers equipped with cooling blocks for refluxing the solvent. Prescribed amounts of the catalyst (0.50 mol% as Ti atom) and cyclooctene (1.0 mmol) in a toluene solution (1.5 cm^3) were taken into a 20 cm^3 glass Schlenk tube under an Ar atmosphere. This mixture was heated and allowed to equilibrate at 60 °C for 10 min. ^{t}BuOOH (1.0 mmol) in decane (1.2 cm^3) was then added by the use of a plastic pipette. The mixture was stirred for 4 h, and the Schlenk tube was cooled rapidly in an ice bath. The products were identified by the use of GC–MS (Shimadzu GC–MS Parvum 2, Zebron ZB-1 capillary column, i.d. 0.25 mm, length 30 m, 50–250 °C) and quantified by gas–liquid chromatography (GL Sciences GC353, Inertcap 17 capillary column, i.d. 0.25 mm, length 30 m, 50–250 °C) using biphenyl as an internal standard.

3. Results and discussion

3.1. Catalytic activity for the epoxidation of cyclooctene

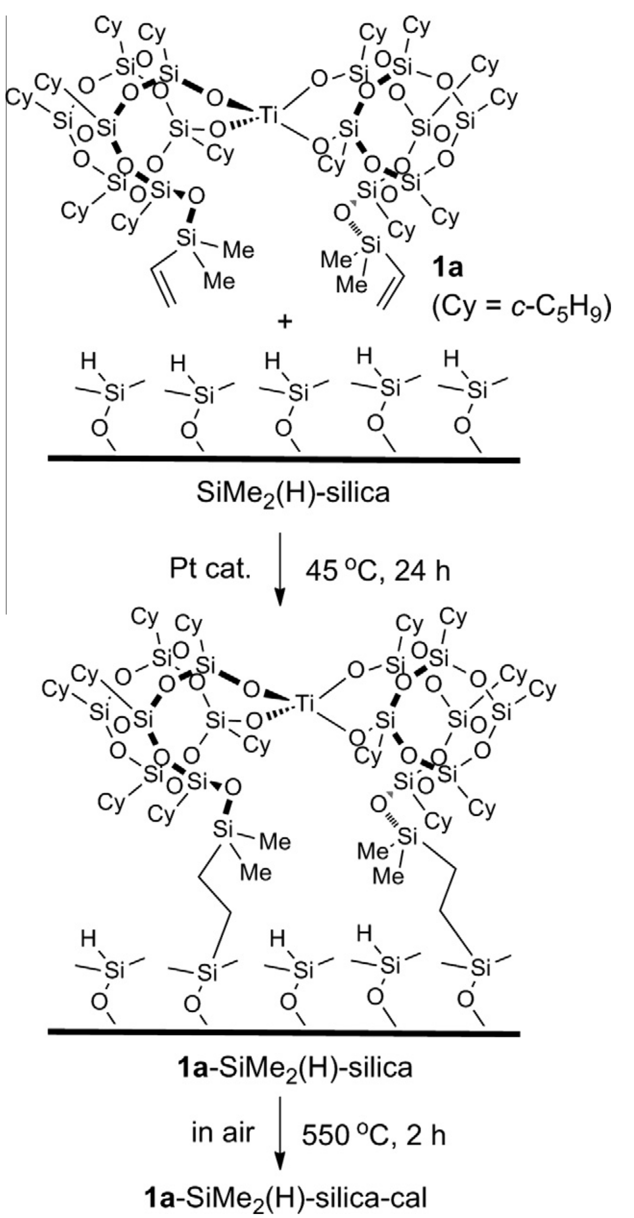
Silica-supported titanium oxide catalysts were prepared by the calcination (550 °C, 2 h) of Ti-containing POSS tethered or supported on various silicas. A silica-tethered catalyst, designated as **1a**-$SiMe_2$(H)-silica (see Scheme 1), was prepared by the Pt-catalyzed hydrosilylative condensation of commercially available dimethylsilyl-functionalized silica with vinylsilyl groups of **1a**. An oxide catalyst, **1a**-$SiMe_2$(H)-silica-cal, was prepared by the calcination of **1a**-$SiMe_2$(H)-silica in air at 550 °C for 2 h. On the other hand, an oxide catalyst designated as **1a**@$SiMe_2$(H)-silica-cal was prepared by the usual impregnation method from a toluene solution of **1a**, followed by calcination.

The activities of these catalysts for the epoxidation of cyclooctene were examined by the use of ^{t}BuOOH as an oxidant (Eq. (1)). The results are summarized in Table 1. In all of the cases examined, cyclooctene oxide was produced selectively, and the formation of byproducts was negligible. For comparison, the activity of **1a** as a homogeneous catalyst was examined, and this produced cyclooctene oxide in yields of 31% and 41% when the reaction was conducted for 1.5 h and 4 h, respectively (entries 1 and 2). Other Ti-containing POSS, **1b** and **2** (see Scheme 2), showed similar activities (entries 3 and 4). The activities of Ti-containing POSS as homogeneous catalysts for the epoxidation by organic peroxides have been previously reported [16–23]. Silica-tethered **1a** showed a catalytic activity similar to that of **1a**, indicating that **1a** was tethered without a loss of activity (entry 5). An oxide catalyst, **1a**-$SiMe_2$(H)-silica-cal, showed a significant activity

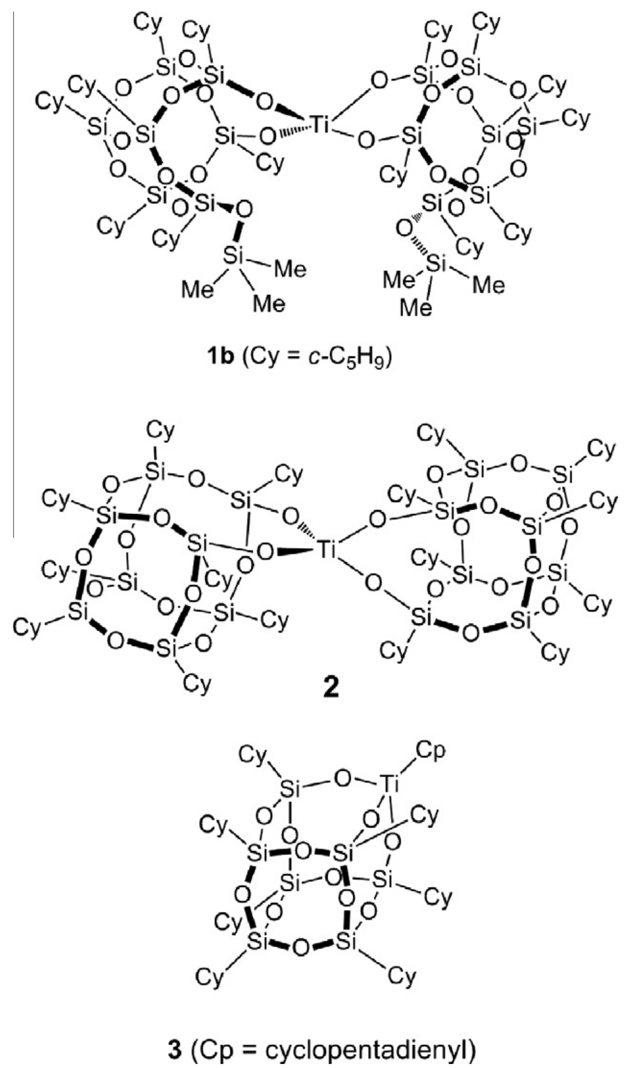
Table 1
Catalytic activity of Ti-containing POSS-based catalyst for the epoxidation of cyclooctene by ^{t}BuOOH.[a]

Entry	Catalyst	Reaction time (h)	Epoxide yield (%)[b]	TOF (h^{-1})
1	**1a** (homogeneous)	4	41	21
2	**1a** (homogeneous)	1.5	31	41
3	**1b** (homogeneous)	1.5	33	44
4	**2** (homogeneous)	1.5	29	39
5	**1a**-$SiMe_2$(H)-silica	4	41	21
6	**1a**-$SiMe_2$(H)-silica-cal	4	70	35
7	**1a**@$SiMe_2$(H)-silica-cal	4	75	38
8	**1a**@$SiMe_2$(H)-silica-cal	1.5	53	71
9	**1b**@$SiMe_2$(H)-silica-cal	4	90	45
10	**2**@$SiMe_2$(H)-silica-cal	4	86	43
11	**3**@$SiMe_2$(H)-silica-cal	4	60	30
12	**4**@$SiMe_2$(H)-silica-cal	4	39	20

[a] The reaction conditions are shown in Eq. (1).
[b] Yield based on cyclooctene determined by GLC.

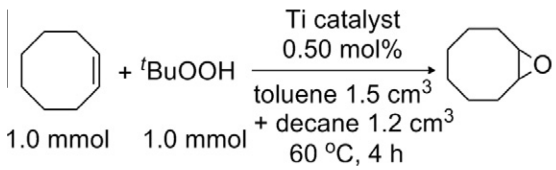


Scheme 1. Preparation of a silica-tethered catalyst and an oxide catalyst.



Scheme 2. Ti-containing POSS used for the preparation of oxide catalysts.

(70%; entry 6) than either the homogeneous or tethered Ti-containing POSS catalysts. Furthermore, an oxide catalyst prepared by the usual impregnation method (**1a**@$SiMe_2$(H)-silica-cal) showed slightly higher activity (yield of epoxide; 75%) than **1a**-$SiMe_2$(H)-silica-cal (entry 7), and a high TOF of 71 h^{-1} was recorded in the reaction for 1.5 h (entry 8). Note that re-examination of the catalytic run shown in entry 7 using the same batch of the catalyst resulted in 78% yield, and the reaction using another batch of **1a**@$SiMe_2$(H)-silica-cal afforded the epoxide in 79% yield. These results indicate good reproducibility of the results in the present system.



(1)

The above results indicate that the tethering of **1a** through covalent bonding did not improve the activity of the resulting catalyst. Therefore, we examined the effects of titanium sources on the activity of the catalysts prepared by the impregnation method. As shown in entries 9 and 10, oxide catalysts prepared using **1b** and **2** showed higher activities (90% and 86% yields, respectively) than that prepared using **1a**, while the catalyst prepared using a corner-capped Ti-containing POSS (**3**) (see Scheme 2) showed a moderate activity (entry 11), which indicates that Ti-bridged POSS are excellent titanium precursors. The activity of **4**@$SiMe_2$(H)-silica-cal was poor, even though impregnation was performed under an Ar atmosphere to avoid the hydrolysis of **4** caused by contact with moisture (entry 12). The catalyst prepared by the impregnation of **4** in an air atmosphere gave the epoxide in the lower yield (26%). On the other hand, Ti-containing POSS can be safely handled in air, which reflects high stability.

Except for **1a**-$SiMe_2$(H)-silica, these catalysts did not exhibit activity for epoxidation using an aqueous solution of hydrogen peroxide. Severe non-productive decomposition of hydrogen peroxide was observed in the presence of oxide catalysts such as **1a**-$SiMe_2$(H)-silica-cal and **1a**@$SiMe_2$(H)-silica-cal. As reported previously, Ti-POSS do not show activity as homogeneous catalysts when hydrogen peroxide is employed as an oxidizing reagent [23,27]. In aqueous solutions, Ti-POSS molecules severely aggregate, which would be one reason for the lack of the catalytic activity. On the other hand, Ti-POSS catalysts tethered or immobilized onto polydimethylsiloxane [27], mesoporous silica–polymer composites [28], silyl-functionalized silicas [29], and gels composed of POSS molecules [31] were reported to show excellent activities for the epoxidation of alkenes by an aqueous hydrogen peroxide solution. Note that all of these catalysts are heterogeneous and strongly hydrophobic because of the presence of organic groups on their surface. In the present study using oxide catalysts, the active Ti species are present on the hydrophilic surface of the supported oxide catalysts, which would prevent the access of alkenes to the Ti species, and facilitate non-productive decomposition of hydrogen peroxide.

Table 2 shows the effect of the silica support on the catalytic activity for the epoxidation of cyclooctene. **1a** was impregnated onto seven silica supports [MCM-41, Cabosil, and JRC-SIO-1, -5, -6, -7, and -8], and this was followed by calcination at 550 °C. Among the catalysts examined, Cabosil-supported catalysts prepared using Ti-bridged POSS showed the highest activities (83–88% yields for 4 h, entries 1, 9, and 10). A high TOF of 91 h^{-1} was achieved in the reaction for 1.5 h (entry 2). The ICP-AES analysis revealed that no titanium species leached into the solution after the reaction using **1a**@Cabosil-cal (entry 1). **1a**@MCM-41-cal also showed excellent activity to afford the desired epoxide in 81% yield (TOF of 41 h^{-1} for 4 h, entry 3). This activity is comparable to those of MCM-41-based titanium catalysts reported in previous studies [10,25,30,45]. For example, a Ti-MCM-41 catalyst (Si/Ti molar ratio; 100) showed a TON of *ca.* 39 h^{-1} for the epoxidation of cyclooctene by ^{t}BuOOH for 5 h at 60 °C (TON; *ca.* 196 for 5 h) [45]. The activities of the catalysts prepared using JRC silicas were moderate. A Cabosil-supported catalyst derived from **3** showed a slightly lower TOF in the reaction for 1.5 h, 77 h^{-1} (entry 12), compared to that of the catalyst prepared using **1a** (entry 2). Both the Cabosil- and MCM-41-supported catalysts prepared using **4** as a titanium source showed lower activities than the catalysts prepared using **1a**, **1b**, or **2** (entries 13–15).

Table 2
Effect of silica support and Ti precursors for the epoxidation of cyclooctene by ^{t}BuOOH.[a]

Entry	Catalyst	Reaction time (h)	Epoxide yield (%)[b]	TOF (h^{-1})
1	**1a**@Cabosil-cal	4	88	44
2	**1a**@Cabosil-cal	1.5	68	91
3	**1a**@MCM-41-cal	4	81	41
4	**1a**@JRC-SIO-1-cal	4	68	34
5	**1a**@JRC-SIO-5-cal	4	77	39
6	**1a**@JRC-SIO-6-cal	4	71	36
7	**1a**@JRC-SIO-7-cal	4	66	33
8	**1a**@JRC-SIO-8-cal	4	75	38
9	**1b**@Cabosil-cal	4	87	44
10	**2**@Cabosil-cal	4	83	42
11	**3**@Cabosil-cal	4	87	44
12	**3**@Cabosil-cal	1.5	58	77
13	**4**@Cabosil-cal	4	72	36
14	**4**@Cabosil-cal	1.5	46	61
15	**4**@MCM-41-cal	4	53	27

[a] The reaction conditions are shown in Eq. (1).
[b] Yield based on cyclooctene determined by GLC.

It is important to determine whether the reaction actually occurs on the solid surface. Hot filtration of the solid catalyst after the reaction in the presence of **1a**@Cabosil-cal was allowed to proceed at 60 °C for 0.5 h completely suppressed further progress of the reaction (Fig. 1). This result strongly suggests that the catalyst worked heterogeneously.

The epoxidation of a larger alkene, limonene, was performed (Eq. (2)). The epoxidation selectively occurred at the tri-substituted C–C double bond [30]. As shown in Table 3, the Cabosil-supported catalysts prepared using **1a** or **1b** showed slightly higher activity than that of **1a** as a homogeneous catalyst, whereas the catalyst derived from **4** showed the lowest activity. These results suggest the

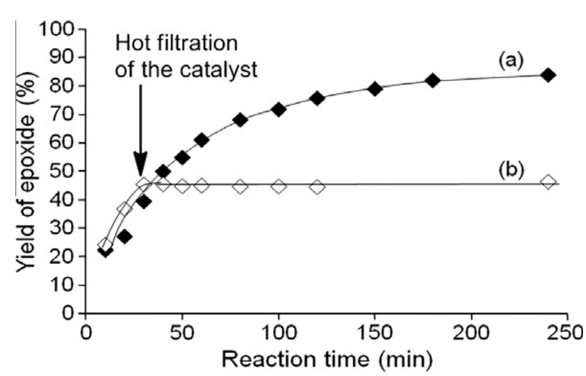


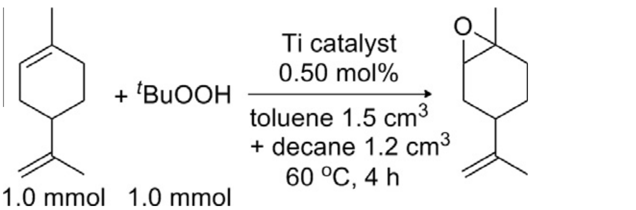
Fig. 1. Time course of the epoxidation of cyclooctene in the presence of **1a**@Cabosil-cal (a) without and (b) with hot filtration of the catalyst 0.5 h after the reaction started.

Table 3
Effect of Ti catalysts for the epoxidation of limonene by ^{t}BuOOH.[a]

Entry	Catalyst	Epoxide yield (%)[b]	TOF (h^{-1})
1	**1a** (homogeneous)	23	12
2	**1a**@Cabosil-cal	27	14
3	**1b**@Cabosil-cal	24	12
4	**2**@Cabosil-cal	22	11
5	**4**@Cabosil-cal	15	8

[a] The reaction conditions are shown in Eq. (2).
[b] Yield based on cyclooctene determined by GLC.

applicability of the supported catalysts for the epoxidation of sterically demanding alkenes.



(2)

One of the major advantages of solid catalysts is the reusability. After the reaction shown in entry 1 of Table 2, the solid catalyst was separated from the reaction mixture by centrifugation and washed three times with toluene (2.0 cm^3). The vacuum-dried catalyst showed slightly lower activity than the fresh catalyst to give the epoxide in 78% yield. Subsequent calcination at 550 °C for 2 h increased the activity of the recovered catalyst and the epoxide was produced in a yield of 81%, indicating that the catalyst was reusable.

3.2. Characterization of the oxide catalysts prepared using Ti-POSS

To examine the effects of Ti-POSS on the properties of the oxide catalysts, characterization was performed by XRD, nitrogen gas adsorption, UV–Vis spectroscopy, and XPS. The powder XRD patterns of all of the catalysts did not show any peaks due to crystalline titanium oxides, indicating that titanium oxide species were highly dispersed on the surface of the catalysts. The UV–Vis spectra reported in Fig. 3 (see below) will be more informative on the local environment of Ti species. Table 4 lists the results of nitrogen adsorption measurements of selected catalysts and supports, and Fig. 2 shows the nitrogen adsorption/desorption isotherms of **1a**-SiMe$_2$(H)-silica, **1a**-SiMe$_2$(H)-silica-cal, **1a**@SiMe$_2$(H)-silica-cal, Cabosil, and **1a**@Cabosil-cal. All of the catalysts supported on SiMe$_2$(H)-silica showed typical type-IV isotherms [49], indicating the presence of mesopores. The isotherms of Cabosil and **1a**@Cabosil-cal were of type-II [49], which indicates the presence of both meso- and macropores. In particular, Cabosil possesses a large macropore volume, which would be one reason for the superior activity of Cabosil-supported catalysts, since macropores are advantageous in terms of diffusion of the substrates and the products.

While the formation of micropores by the calcination of POSS molecules has been previously reported [32–44], an increase in the BET surface area by the calcination of silica-supported POSS was not recognized from the results shown in Table 4, probably because of a low loading level of POSS.

UV–Vis spectroscopy is a very powerful tool for investigating the local structure around titanium species in TiO_2–SiO_2 mixed oxides [50–52]. The LMCT (ligand–metal charge transfer) transition from O to Ti in isolated tetrahedral titanium species is usually observed at a shorter wavelength compared to that of octahedral titanium species. For example, the LMCT transitions of TS-1 and other titanosilicates are observed at 200–220 nm and are assigned to isolated tetrahedral titanium species [53]. Fig. 3 shows the UV–Vis diffuse reflectance spectra of selected catalysts under dehydrated conditions. The oxide catalyst, **1a**@SiMe$_2$(H)-silica-cal, showed a sharp band at 220 nm. **1a**-SiMe$_2$(H)-silica-cal showed a peak that was very similar to that of **1a**@SiMe$_2$(H)-silica-cal. These spectra closely resemble those reported for titanosilicates [50,52], and this result clearly indicates that both **1a**-SiMe$_2$(H)-silica-cal and **1a**@SiMe$_2$(H)-silica-cal contain isolated tetrahedral titanium species on their surface. The Cabosil- and MCM-41-supported catalysts prepared using **1a** also showed absorption at around 220 nm. On the other hand, **3**@SiMe$_2$(H)-silica-cal and **4**@SiMe$_2$(H)-silica-cal both showed a major band at around 260 nm, which has been assigned to octahedral titanium species [51], together with shoulders at 225 nm and 310 nm. The former shoulder is considered to be due to isolated tetrahedral titanium species, and the latter is due to $[TiO_2]_n$ clusters [54]. These results suggest the formation of octahedral titanium ions in oxide clusters on the surface of **3**@SiMe$_2$(H)-silica-cal and **4**@SiMe$_2$(H)-silica-cal. The spectrum of **4**@Cabosil-cal showed very similar to those of **3**@SiMe$_2$(H)-silica-cal and **4**@SiMe$_2$(H)-silica-cal.

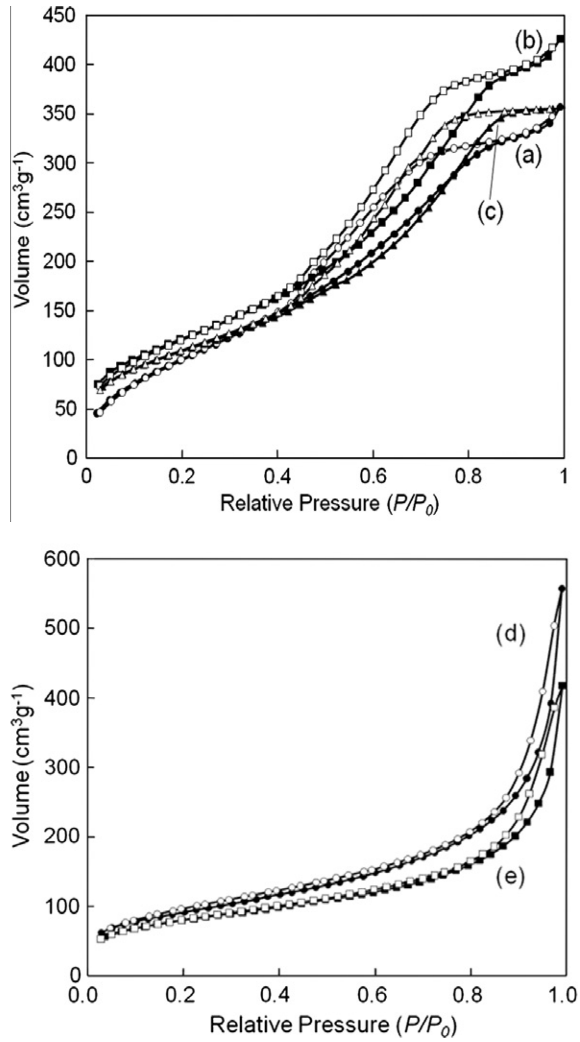


Fig. 2. Nitrogen adsorption/desorption isotherms of (a) **1a**-SiMe$_2$(H)-silica, (b) **1a**-SiMe$_2$(H)-silica-cal, (c) **1a**@SiMe$_2$(H)-silica-cal, (d) Cabosil, and (e) **1a**@Cabosil-cal. Filled and open symbols show adsorption and desorption data, respectively.

The XPS study revealed the presence of Ti(IV) species on the surface of all of the catalysts examined. Fig. 4 shows selected results. Remarkably, **1a**@SiMe$_2$(H)-silica-cal showed a Ti 2p$_{3/2}$ band

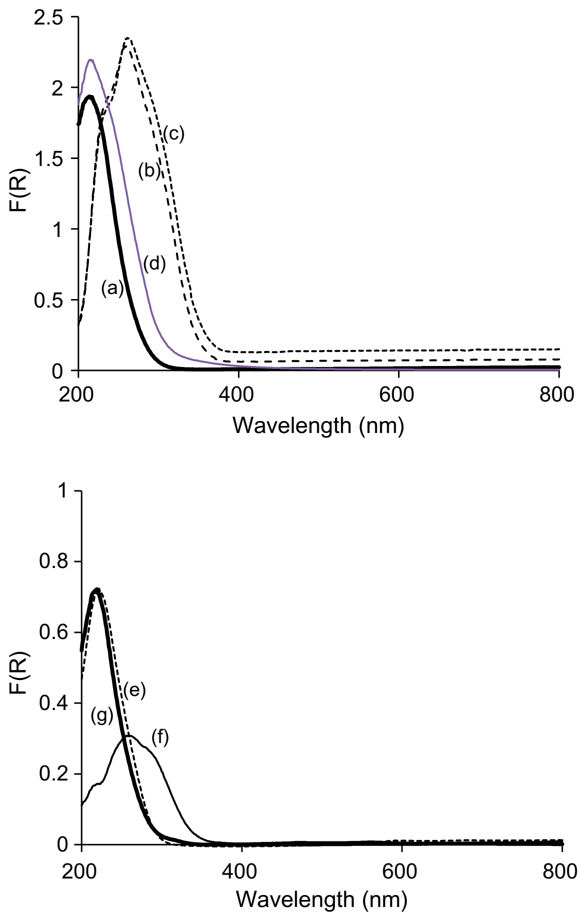


Fig. 3. UV–Vis diffuse reflectance spectra of (a) **1a**@$SiMe_2$(H)-silica-cal, (b) **3**@$SiMe_2$(H)-silica-cal, (c) **4**@$SiMe_2$(H)-silica-cal, (d) **1a**-$SiMe_2$(H)-silica-cal, (e) **1a**@Cabosil-cal, (f) **4**@Cabosil-cal, and (g) **1a**@MCM-41-cal.

Table 4
Summary of the results of nitrogen adsorption measurements of the selected catalysts and supports.

Catalyst	BET S.A. ($m^2\ g^{-1}$)	Mean pore diameter (nm)[a]	Total pore volume ($cm^3\ g^{-1}$)
$SiMe_2$(H)-silica	394	6.0	0.55
$SiMe_2$(H)-silica-cal	420	5.9	0.62
1a-$SiMe_2$(H)-silica	410	5.4	0.55
1a-$SiMe_2$(H)-silica-cal	444	5.9	0.66
1a@$SiMe_2$(H)-silica-cal	394	5.6	0.55
1b@$SiMe_2$(H)-silica-cal	399	5.7	0.57
2@$SiMe_2$(H)-silica-cal	396	5.6	0.55
3@$SiMe_2$(H)-silica-cal	413	5.8	0.60
4@$SiMe_2$(H)-silica-cal	409	5.8	0.59
Cabosil	320	10.8	0.86
1a@Cabosil-cal	276	9.4	0.65
4@Cabosil-cal	303	9.3	0.71
MCM-41	1396	2.6	0.90
1a@MCM-41-cal	1405	2.4	0.83

[a] The mean pore diameter was calculated from the pore volume and the specific surface area assuming that the pore was cylindrical.

at 460.0 eV, which is significantly higher than those of **3**@$SiMe_2$(H)-silica-cal and **4**@$SiMe_2$(H)-silica-cal (458.5 eV). Since Ti $2p_{3/2}$ peaks centered at *ca.* 460 eV and 458–459 eV have been assigned to a framework tetrahedral titanium and an extraframework octahedral titanium phase for titanosilicates, respectively [53,55,56], the present result is consistent with the formation of tetrahedral titanium species on the surface of **1a**@$SiMe_2$(H)-silica-cal.

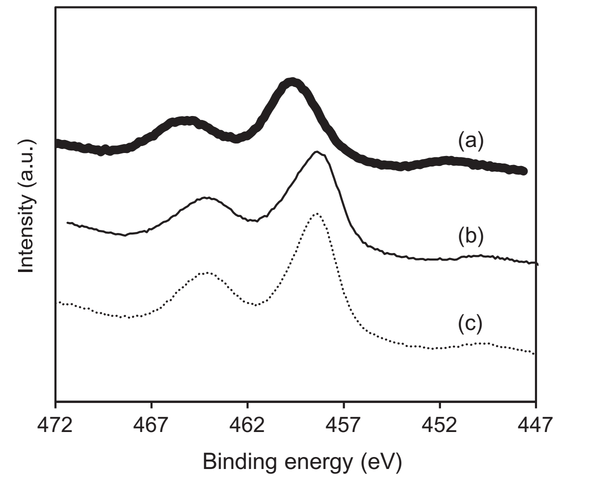


Fig. 4. Ti 2p spectra of (a) **1a**@$SiMe_2$(H)-silica, (b) **3**@$SiMe_2$(H)-silica-cal, and (c) **4**@$SiMe_2$(H)-silica-cal.

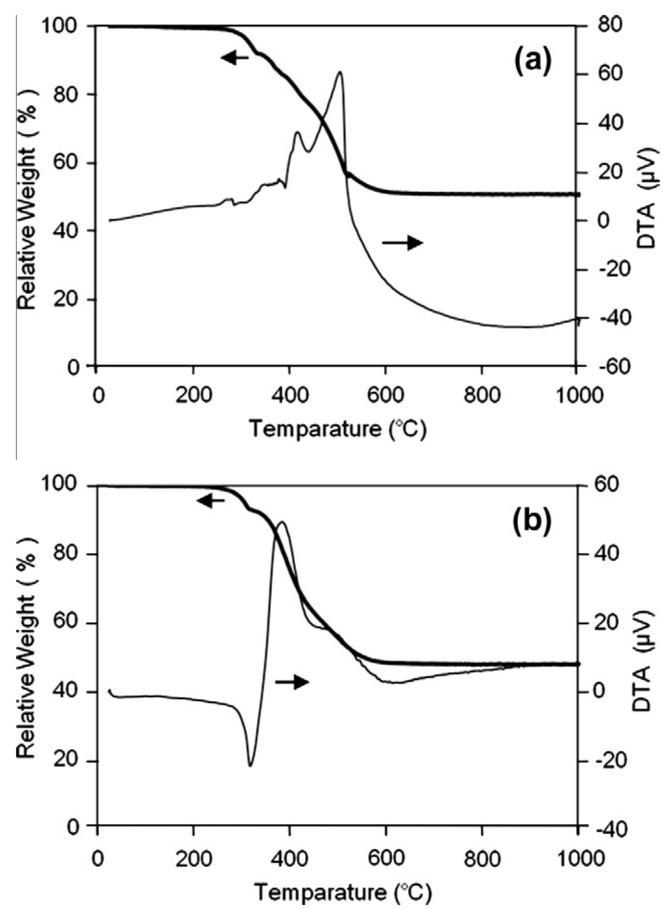


Fig. 5. TG-DTA profiles of (a) **1a** and (b) **3** in a stream of air.

Changes in the structures of Ti-POSS during calcination were investigated by TG-DTA, DRIFT, and NMR measurements. Since several POSS have been reported to be volatile in spite of their relatively large molecular weights [6,7,9], the loss of Ti and Si species during the calcination of Ti-POSS was examined by treating **1a**, **1b**, **2**, and **3** in air at 550 °C for 2 h in the box furnace. The ceramic yields of SiO_2–TiO_2 from **1a** (49.6%) and **1b** (49.4%) were slightly lower than the theoretical values (53.0% and 53.8% for **1a** and **1b**, respectively). The XRF analyses showed that Si/Ti atomic ratios of the resulting oxides from **1a** and **1b** were 14.8(±0.2) and 14.9(±0.1), respectively. These results indicate that by the calcination of both Ti-POSS, 7(±1)% of Si was lost, while 100(±2)% and 99(±1)% of Ti was remaining in the resulting oxides from **1a** and **1b**, respectively. During the calcination of **1a** and **1b**, trimethylsilyl or dimethylvinylsilyl groups in **1a** or **1b** would be cleft at relatively low temperature and then sublime, as revealed by the TG study (see below). On the other hand, the ceramic yields of oxides from **2** (52.5%) and **3** (51.0%) were very close to the theoretical values (51.6% and 50.8%, respectively). These results indicate the absence of loss of Ti species during the calcination of POSS at 550 °C for 2 h.

As shown in Fig. 5, the TG-DTA study demonstrated the stepwise decomposition of **1a** and **3** in an air stream. Note that TG-DTA measurements of supported Ti-POSS did not give any distinct TG and DTA responses, probably because of the low loading levels. For **1a**, decreases in weight by 7% and 42% were observed at 300–350 °C and 400–600 °C, respectively. A slightly exothermic decrease at 300–350 °C would be due to the oxidative cleavage of dimethylvinylsilyl groups, and a significant loss of weight above 400 °C is due to the combustion of cyclopentyl groups. The decomposition of **3** also proceeded in a stepwise manner: an initial endothermic loss of weight by 6% at *ca.* 315 °C and a significantly exothermic loss above 320 °C.

The DRIFT spectra of **1a** and **3** treated in air at various temperatures are shown in Fig. 6. While the spectrum of uncalcined **1a** showed strong C–H stretching vibrations due to cyclopentyl groups at 2950 cm^{-1} and 2870 cm^{-1}, these bands almost disappeared above 350 °C. This result is consistent with that of the TG-DTA study, which indicates the combustion of organic substituents in this temperature range. In the spectrum of **3**, a C–H out-of-plane bending vibration band characteristic of a Cp group is observed at about 806 cm^{-1}. This peak disappeared when the sample was heated to 300 °C. This result supports the argument on the TG study, which indicated the decomposition of the Cp group of **3** at this temperature range. Again, C-H stretching vibrations of aliphatic C–H bonds disappeared above 350 °C because of the complete combustion of organic groups. Note that a broad, strong band at about 940 cm^{-1} is observed for the spectra of both **1a** and **3** above 350 °C, which is often reported to be a good fingerprint of the existence of framework titanium species in titanosilicates [51,57,58].

Loss of the Cp group from **3** at around 300 °C was also confirmed by ^{1}H and ^{13}C NMR studies. The treatment of **3** at 300 °C for 10 min (heating rate 10 °C min^{-1}) in an air stream gave a slightly brownish powder, which was soluble in $CDCl_3$ except for a trace amount of brown solid. In the ^{1}H NMR spectrum, the peak of a Cp ring (6.43 ppm) completely disappeared, while resonances attributed to cyclopentyl groups remained. The ^{13}C NMR spectrum did not show the peak assignable to the Cp ring of **3**.

As shown in the first part of the present study, the oxide catalysts prepared using **1a**, **1b**, and **2** as titanium sources showed activities superior to those prepared from **3** and **4**. The combined

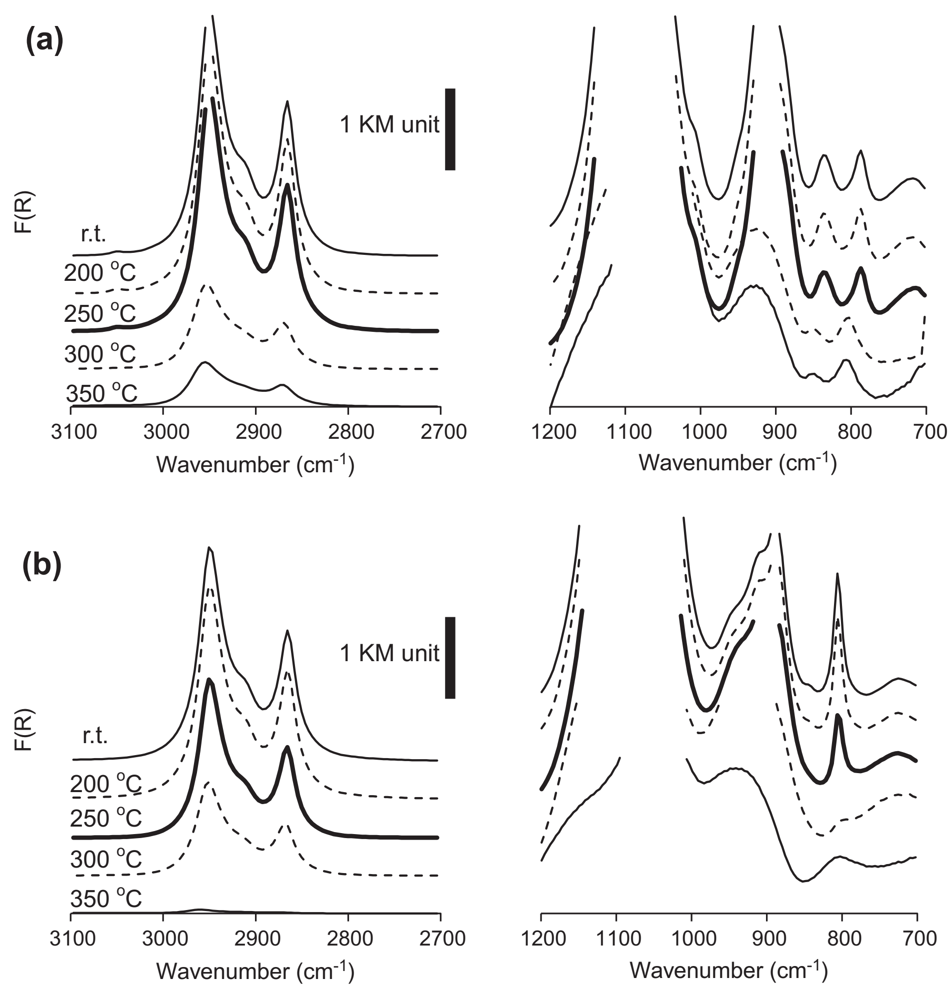


Fig. 6. DRIFT spectra of (a) **1a** and (b) **3** recorded in air at elevated temperatures. Samples were diluted by KBr to be *ca.* 10 wt.%, and spectra in the region exceeding three Kubelka–Munk units are omitted.

results of characterization clearly indicate the selective formation of isolated tetrahedral titanium(IV) species on the surface of the oxide catalysts from **1a**, **1b**, and **2**, and such titanium species would be responsible for the high catalytic activity. Therefore, Ti-bridged POSS are expected to act as precursors of "titanosilicate-like" species. One common feature of **1a**, **1b**, and **2** is that the titanium atom is surrounded by bulky POSS cages through four Ti–O–Si bonds. During calcination, these POSS moieties would be transformed into small silica clusters, which might act as an inorganic separator of titanium species [43,44]. This would prevent the aggregation of titanium oxide species and thus promote the formation of isolated titanium(IV) species on the silica surface. Note that the TG-DTA study of **3** revealed that the Cp (cyclopentadienyl) group decomposed at around 315 °C, which is a lower temperature than that for the combustion of cyclopentyl groups (*ca.* 400 °C). The loss of the Cp group from **3** in the present study might enable the aggregation of Ti species.

4. Conclusion

Silica-supported titanium oxide catalysts with excellent activities for the epoxidation of cyclooctene by ^{t}BuOOH were prepared by the calcination of Ti-bridged POSS supported or tethered on silica at 550 °C. Based on the results of catalytic runs and spectroscopic analyses of the catalysts, highly isolated tetrahedral titanium(IV) species were revealed to be produced on the catalyst surface from **1a**, **1b**, or **2**, while aggregated titanium species were produced from a corner-capped-type Ti-POSS (**3**) and tetraisopropoxytitanium (**4**). These catalysts were also applicable for the epoxidation of limonene. The present study clearly indicates the utility of Ti-bridged POSS as promising precursors for titanosilicate-like active titanium species, which can be implanted on a variety of oxide supports. The present results suggest that compounds that include a titanium atom surrounded by bulky inorganic moieties through four Ti–O–Si bonds may be suitable precursors for epoxidation catalysts. Further attempts to improve the catalytic activities of these catalysts and the application to the epoxidation of much bulky alkenes, as well as the development of much more efficient titanium precursors, are underway.

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