

Supporting Information

Facile Preparation of Silica-supported Ti Catalysts Effective for the Epoxidation of Cyclooctene using Ti-bridged Silsesquioxanes

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Experimental procedures and analytical data

Contents:

1. General considerations
2. Experimental procedures
3. Effect of the amount of silica on Ti-POSS-catalyzed epoxidation
4. Characterization of silica-supported Ti catalysts
5. NMR study of the reaction of Ti-POSS and the POSS trisilanol
6. References

1. General considerations

Materials and Methods.

Ti-containing POSS were prepared, and subsequent manipulations were performed, under an argon atmosphere using standard Schlenk techniques. Dehydrated toluene (Wako), cyclooctene (Nacalai Tesque), and ^tBuOOH in a decane solution (5.5 M, Fluka) were used as received. $\text{Ti}[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_2\text{R})]_2$ (**1a**; R = vinyl, **1b**; R = methyl) and $\text{Ti}[(c\text{-C}_5\text{H}_9)_8\text{Si}_8\text{O}_{13}]_2$ (**2**) were synthesized based on the methods described in a previous report [1]. Tetrakis(dimethylamido)titanium (Aldrich), $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OH})_3$ (Aldrich), $(c\text{-C}_5\text{H}_9)_8\text{Si}_8\text{O}_{11}(\text{OH})_2$ (Aldrich), $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OH})_2(\text{OSiMe}_2\text{R})$ (R = vinyl, methyl, Aldrich), and $(c\text{-C}_4\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OH})_3$ (Aldrich) were obtained commercially and used without further purification. Cabosil (Cabot, HS-5) was used as received. SBA-15 [2] and MCM-41 [3] was prepared based on the method described in the literature. Ceria was prepared by treating a solution of cerium(III) nitrate hexahydrate with aqueous ammonia followed by calcination at 400 °C for 30 min, as described elsewhere [4]. Zirconia and magnesia were prepared by a method similar to that used to obtain ceria from zirconium(IV) dinitrate oxide and magnesium nitrate, respectively (for zirconia, calcination temperature; 500 °C). JRC silicas, JRC-TIO-4, and JRC-ALO-8 were obtained from the Catalysis Society of Japan. Cabosil and JRC silicas were evacuated at room temperature for *ca.* 30 min just before use unless otherwise noted, while SBA-15 and MCM-41 were calcined in air at 500 °C for 6 h and at 550 °C for 4 h, respectively. Characterization data of JRC silicas have been reported before [5-8].

Physical and Analytical Measurements.

The supported catalysts were analyzed by nitrogen gas adsorption, UV-visible spectroscopy, X-ray photoelectron spectroscopy (XPS), and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). 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 under the assumption that the pore was cylindrical. UV-visible 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). The spectra were taken in a UV cell under air without any pretreatment. Barium sulfate (Nacalai Tesque) was used as a reflectance standard, and all the spectra were modified in terms of the Kubelka-Munk function. 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 $K\alpha$ radiation (1254 eV) generated by an X-ray tube operating at 15 kV, 400 W. The electron take-off angle was set at 45 deg. Binding energies were referenced to the C 1s level of residual graphitic carbon and/or Si 2p level of silicas [9]. The titanium contents in the catalysts and the leaching of titanium species from the catalysts during the reaction were investigated by an ICP-AES analysis using a Shimadzu ICPS-1000III analyzer.

2. Experimental Procedure

Preparation of silica-supported Ti catalysts from a mixture of Ti-containing POSS and silica.

A mixture of Ti- POSS (**1a**, **1b**, or **2**) (0.050 mmol) and silica (Cabosil or JRC-SIO-8) (1.0 g) in toluene (20 cm³) was refluxed (bath temp. 120 °C) with stirring in air for 48 h. After filtration, the resulting solid was washed three times with toluene (10 cm³) in air and subsequent vacuum-drying afforded a supported catalyst, which is hereafter referred to as **1a**/Cabosil.

Catalytic epoxidation of alkenes. All reactions were performed with the use of hot stirrers equipped with cooling blocks for refluxing the solution. A typical procedure is as follows. An appropriate catalyst (0.50 mol% as Ti atom), cyclooctene (1.0 mmol) in toluene solution (1.5 cm³), and, when necessary, oxide additives (90 mg) were taken into a glass Schlenk tube under an Ar atmosphere. The reaction mixture was heated by a heating block and allowed to equilibrate at 60 °C for 10 min. ^tBuOOH (1.0 mmol) in a decane solution (1.2 cm³) was then added by the use of a plastic pipette. The mixture was stirred for 4 h under Ar and then cooled rapidly in an ice bath (Condition **A**). For the reactions under Condition **B**, 2.0 cm³ of cyclooctene (3.0 M) in toluene and ^tBuOOH (5.5 M) in decane were used. 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 (10 °C min⁻¹)) and quantified by gas-liquid chromatography (Shimadzu GC-14APF, Zebron ZB-1 capillary column, i.d. 0.25 mm, length 30 m, 50–250 °C (10 °C min⁻¹)) using biphenyl as an internal standard.

After the reaction, the **1a**/JRC-SIO-8 catalyst was separated from the reaction mixture by centrifugation and washed with 2 cm³ of toluene, and then subjected to reuse.

Reactions of Ti-POSS with POSS silanols. To an LPV NMR tube (Willmad) were added Ti-POSS (0.010 mmol), POSS silanol **3** (0.030 mmol), hexamethylbenzene (*ca.* 0.0050 mmol, an internal standard), and toluene-*d*₈ (Acros). After degassing by a freeze-and-thaw process, the sample was subjected to suitable heat treatment and measurements.

3. Effect of the amount of silica on Ti-POSS-catalyzed epoxidation

As shown in Table S1, the addition of 50–200 mg of JRC-SIO-8 was found to effectively promote the epoxidation of cyclooctene in the presence of a catalytic amount of **1a** (Ti catalyst 0.0050 mmol, cyclooctene 1.0 mmol, TBHP 1.0 mmol, 60 °C).

Table S1. Effects of the amount of JRC-SIO-8 on the epoxidation of cyclooctene catalyzed by **1a**

Entry	Amount of JRC-SIO-8 (mg)	Yield of epoxide after 90 min (%) ^a	Yield of epoxide after 4 h (%) ^a
1	0	31	41
2	10	53	70
3	50	67	82
4	90	79	91
5	200	69	86

^a Determined by GLC.

4. Characterization of silica-supported Ti catalysts

i) UV–visible diffuse reflectance spectra

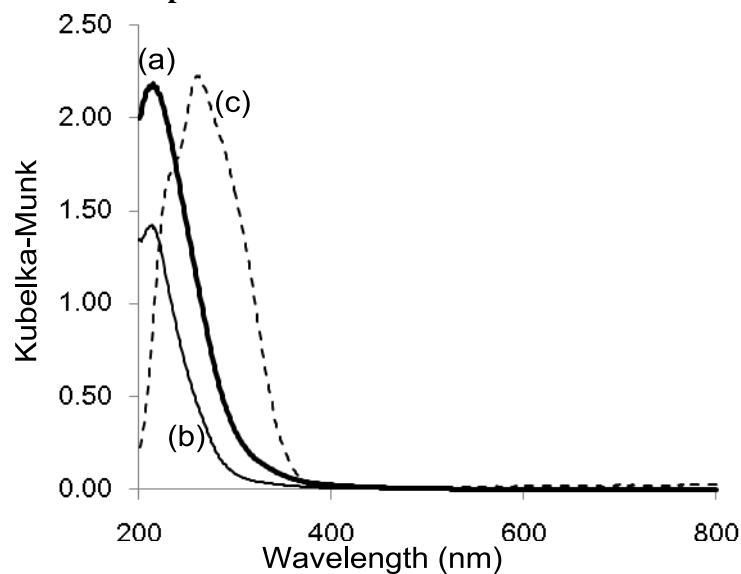


Fig. S1 UV–visible diffuse reflectance spectra of (a) **1a**/JRC-SIO-8, (b) **2**/JRC-SIO-8, and (c) Ti/Cabosil.

ii) XPS results

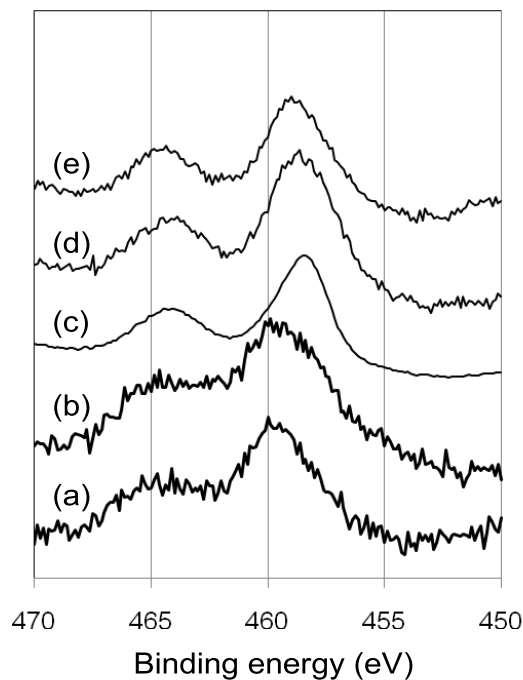


Fig. S2 Ti $2p_{5/2}$ XP spectra of (a) **1a**/JRC-SIO-8, (b) **2**/JRC-SIO-8, (c) Ti/Cabosil, (d) **1a**, and (e) **2**.

5. NMR study of the reaction of Ti-POSS and the POSS trisilanol

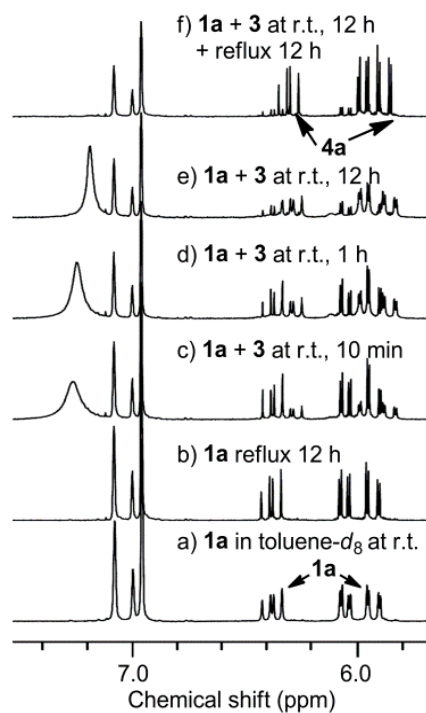


Fig. S3 ^1H NMR spectra of the reaction between **1a** and **3** in toluene- d_8 .

6. References

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