Surface Functionalization of Supported Mn Clusters to Produce Robust Mn Catalysts for Selective Epoxidation

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Supporting Information

ABSTRACT: A robust heterogeneous Mn catalyst for selective epoxidation was prepared by the attachment of a Mn4 oxonuclear complex \([\text{Mn}_4\text{O}_2(\text{CH}_3\text{COO})_7(\text{bipy})_2](\text{ClO}_4)\cdot 3\text{H}_2\text{O})\) (1) on SiO2 and the successive stacking of SiO2-matrix overlayers around a supported Mn cluster. The structures of supported Mn catalysts were characterized by means of FT-IR spectroscopy, diffuse-reflectance UV/vis spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, and Mn K-edge X-ray absorption fine structure. A ligand exchange reaction between the CH3COO ligand of 1 and surface silanol group produced a SiO2-supported Mn cluster (2), whose coordination structure was similar to 1. Subsequent heating of 2 under vacuum yielded supported Mn clusters (3, 4) through the partial elimination of CH3COO ligands. The surface-attached Mn clusters of 2, 3, and 4 were easily released to a reaction solution under epoxidation conditions (Mn leaching: approximately 50%), although they were active for epoxidation of trans-stilbene (the conversion of trans-stilbene, 99%, and the selectivity of trans-stilbene epoxide, 96%, for 6 h on 3). We found that the functionalization of the supported Mn cluster on 2 with surface SiO2-matrix overlayers altered the reactivity of the supported Mn cluster. Dimeric Mn species (5c) with reduced Mn oxidation state and coordination numbers was formed together with a reaction nanospace surrounded by the SiO2-matrix overlayers. By optimizing the stacking manner of the SiO2-matrix overlayers, the durability of the Mn catalyst was remarkably improved from leaching (the Mn leaching reached the minimum value of 0.01%), and active and stable epoxidation performances were successfully achieved in the heterogeneous phase (the conversion of trans-stilbene, 97%, and the selectivity of trans-stilbene epoxide, 91%, for 31 h on 5c).

KEYWORDS: Mn cluster, SiO2 particles, surface functionalization, SiO2-matrix overlayers, selective epoxidation

1. INTRODUCTION

Creating a new catalytically active and stable species from transition metal complexes and clusters remains a fundamental challenge in catalysis. The catalytic properties of homogeneous transition metal complexes can be fine-tuned by using various combinations of metal ions and ligands at a molecular level.1 However, coordination structures are likely to decompose during the homogeneous catalytic reaction conditions and tend to lose catalytic activity, for instance, through aggregation of metal complexes forming inactive species.

The heterogenization of homogeneous metal complexes and clusters by grafting or anchoring to a solid surface, or by immobilizing in polymers or porous materials, has been widely adopted to produce more stable metal complexes during catalytic reaction as well as to produce unique catalytically active metal species.2,3 The site isolation effect on solid surfaces prevents metal complexes and clusters from undergoing aggregation that will result in deactivation, and makes them easier to separate from reaction media for recycling.2,3 However, the chemical grafting of a metal complex on a support does not always give a stable catalytically active metal species, and leaching of the metal species from the surface often proceeds under catalytic reaction conditions. This phenomenon occurs when chemical bonding between a metal complex and an oxide surface is relatively weak and does not last sufficiently long under the catalytic conditions.

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One notable example is a catalyst system using 3d-metal complexes (Mn and Fe) under oxidation reaction conditions. Mn complexes and clusters,4 such as Mn porphyrines,5 Mn salens,6 and Mn 1,4,7-triaza-1,4,7-trimethylocyclophanone (tmtacn) complexes,7 were reported to be promising oxidation catalyst precursors because their derivatives exhibit high activity and selectivity for oxidation of alkenes and alcohols. In some cases, they could be used with mild oxidants such as O2 and H2O2. Mn oxo-nuclear clusters with acetate and phosphate ligands have attracted considerable attention because they were potential models of metal enzyme active sites,8 such as catalase9 and the water oxidation center in Photosystem II.10

The activity for oxidation of alcohols,11 epoxidation and cis-dihydroxylation of alkenes,12−17 hydrogenation,18 and oxidation of alkanes19 were reported. In spite of these intriguing properties, Mn complexes and clusters tend to decompose and lose their catalytic activities in homogeneous conditions.

The heterogenization of Mn complex catalysts has also been investigated with the aim to increase catalytic activity and catalyst stability. Grafting of Mn porphyrine and salen complexes inside mesoporous materials was among the first methods used to prepare heterogeneous Mn complex catalysts. Various supports were used for this purpose, including zeolites,15 mesoporous SiO2,16 clays,17 zinc−aluminum double hydroxides18 and carbon.19 However, Mn species sometimes leached into the solution phase. Covalent anchoring of Mn salen complexes on oxide surfaces or inside mesoporous materials via organic linkers was reported to be effective for dramatically enhancing their stability and recyclability in oxidation reactions without changing the structure of Mn complexes.20 Coordination of Mn ions to surface-functionalized ligands yielded site-isolated supported Mn complex catalysts that were highly stable for epoxidation reactions.21 Grafting of a Mn(tmtacn) dinuclear cluster on a carboxylate-functionalized oxide surface enabled in situ production of a catalytically active Mn dinuclear cluster with a degree of stability.22 Other efficient reported approaches for heterogenization were the incorporation of Mn complexes inside polymers, ionic liquids, and metal−organic frameworks.23−25 The grafted- or supported Mn complexes introduced here had basically similar structures to precursor complexes; therefore, the generation of totally new catalytically active Mn species from the original Mn complexes was quite rare.

Here we report a new catalytically active Mn species through functionalization of a Mn cluster-attached SiO2 surface toward robust epoxidation catalysis in a heterogeneous phase. A Mn oxotetranuclear cluster, [MnO2(CH3COO)2(bipy)2](ClO4)−·3H2O (1),26a which has been prepared as a series of model complexes for Photosystem II,26b,c was chemically attached on the surface of SiO2 particles by reaction with surface Si−OH groups. However, the chemical bond attaching the complex at the interface was found to be easily cleaved under epoxidation reaction conditions. We functionalized the Mn cluster-attached SiO2 surface by stacking SiO2-matrix overlayers through the method we have developed, and the space around the supported Mn cluster was filled by the matrix overlayers. This surface functionalization remarkably changed the epoxidation performances of the Mn catalyst on the SiO2 surface, and the robust epoxidation performances were achieved on the Mn catalyst in a heterogeneous phase.

2. EXPERIMENTAL SECTION

2-1. Preparation of [Mn4O2(CH3COO)7(bipy)2](ClO4)·3H2O (1). All reagents were purchased from Sigma-Aldrich, STREM, Wako Chemicals, and Tokyo Kasei Kogyo, and used as received unless otherwise noted. [Mn4O2(CH3COO)7(py)2](ClO4)− was prepared by the literature method28 and [Mn4O2(CH3COO)7(bipy)2](ClO4)·3H2O (1) was synthesized by literature reported procedure with modifications.26a

Under N2 atmosphere, 2,2′-bipyridine (bipy) (1.15 g, 7.36 mmol) was added to a stirred MeCN solution (50 mL) of [Mn4O2(CH3COO)7(py)2](ClO4)− (2.06 g, 2.36 mmol). The solution was stirred at room temperature for 1 h, and the resulting deep red solution was mixed with a 1:1 mixture of hexane and Et2O (50 mL) and additional Et2O (20 mL). The powder was collected by filtration, washed with Et2O and dried; yield 70.9% (from Mn basis). Compound I was obtained as a dark red powder in trihydrate form. Anal. Calcd for C34H37O16N4Mn4: C, 36.11; H, 3.83; N, 4.95s. Found: C, 36.29; H, 3.65; N, 5.14. 1H NMR (CDCl3): −130.5, −77.0, −29.7, −19.3, −18.8, −11.5, 20.2, 22.8, 28.0, 33.2, 36.4, 45.2. ESI-TOF MS (CH2Cl2): m/z 976.9320 [M]+ (Calcd for C34H37O16N4Mn4, 976.9727) (Supporting Information, Figure S1).

2-2. Preparation of SiO2-Supported Mn4 Cluster (2). SiO2 (1 g, Aerosil 200, Degussa, surface area: 200 m2 g−1) was calcined at 673 K for 2 h and kept under vacuum for 0.5 h prior to the grafting of I. The precalcined SiO2 (1 g) was suspended in CH3Cl (20 mL) under N2, and a CH3Cl solution (10 mL) of I (0.114 g, 1.01 × 10−4 mol) was added. After stirring for 0.5 h, the solvent was removed under reduced pressure, and the resulting solid was allowed to dry under vacuum for another 1−2 h. Loading of Mn was evaluated by X-ray fluorescence (XRF) to be 2.2 wt %, which corresponded to the surface density of 1 to be 0.3 nm−2 (approximately one-third of the maximum surface density). Catalyst 2 with low Mn loading (surface density of 1: 0.2 and 0.1 nm−2) was prepared in a similar way. Catalysts heated for 3 h at 373 and 413 K under vacuum were also prepared (3 and 4).

2-3. Stacking of SiO2-Matrix Overlayers. A SiO2 matrix protecting Mn catalyst (5a) was prepared as follows. Tetramethoxysilane (TMOS, Si(OCH3)4) (0.67 g (0.65 mL)) and distilled H2O (0.27 mL) were placed in glass reactors connected to a two-necked flask containing a supported Mn cluster (2, 0.2 g). After the whole system was evacuated to prepare a closed system with reduced pressure, the glass reactors were heated to 393 K and chemical vapor deposition (CVD) was used to vaporize TMOS and H2O and deposit them on a supported Mn cluster catalyst. During the CVD process, the catalyst was vigorously stirred at room temperature. Then, the two-necked flask was separated from the glass reactor while maintaining the closed system, and hydrolysis−polymerization of TMOS was performed at 358 K for 24 h. The whole closed system was subsequently evacuated at 373 K for 4 h. A Mn catalyst protected by a SiO2 matrix (5b) was prepared in a similar way with double the amounts of TMOS (1.34 g) and H2O (0.54 mL). A Mn catalyst protected by a SiO2 matrix (5c) was prepared by twice performing the procedure of stacking SiO2-matrix overlayers of TMOS (0.67 g) and H2O (0.27 mL). Weight gain after the hydrolysis-polymerization was measured after evacuation at 373 K, and the ratio of polycondensed TMOS was estimated.
2.4. Preparation of SiO2-Supported MnOx Catalysts. 2 was heated for 3 h at 673 K under vacuum to prepare catalyst 6. Catalyst 7 was prepared by the stacking of SiO2-matrix overlayers on 6 similar to the preparation of 5c.

2.5. Catalyst Characterization. XRF was measured on a JEOL JSX-3400RII spectrometer. The loading of Mn on the solid samples was determined by using standard curves of Mn Kα and Si Kα. The amount of CH3COO ligands released from Mn clusters during the attachment to SiO2 was determined as follows. After the impregnation of SiO2 with 1 in a Schlenk tube under N2 atmosphere, the resulting supernatant was decanted from the suspension, and the released CH3COOH was dissolved and quantified by gas chromatography using a flame ionization detector (FID-GC; Shimadzu GC-14B, CHIRALDEX B-DM column). The number of CH3COO ligands in 2, 3, 4, and 5c were determined as follows. The catalysts were treated with excess amount of CF3COOH in CH2Cl2 solution, and the removed CH3COOH was quantified by FID-GC (Shimadzu GC-14B, CHIRALDEX B-DM column).

FT-IR spectra were recorded in transmission mode with 4 cm−1 resolution on a JEOL JIR-7000 spectrometer. A KBr disk of Mn4 cluster (1) was evacuated under vacuum for 1 h in an in situ IR cell equipped with NaCl windows before FT-IR measurements. FT-IR spectra of 2, 3, 4, and 5c were measured under in situ conditions using a neat disk of 2 prepared under N2 atmosphere. The sample was evacuated for 1 h, and the spectrum of 2 was recorded. Then the sample was heated under vacuum for 1 h at 373 K and that of 3 was recorded. Finally, it was heated under vacuum for 1 h at 413 K and that of 4c was recorded.

Transmittance and diffuse-reflectance (DR) UV/vis spectra were recorded on a JASCO V-550-DS spectrometer equipped with an integrating sphere. 1 was dissolved in CH2Cl2. Solid 2, 3, 4, and 5c were placed in quartz cells under Ar atmosphere. 29Si solid-state magic angle spinning (MAS) NMR spectra were recorded on a JEOL JNM-ECX400 spectrometer operating at 79.5 MHz. A single-pulse detection method was used in 29Si NMR measurements, and a sample was set in a zirconia rotor of 4 mm in diameter and rotated at 10 kHz with a relaxation delay time of 3 s. Sodium 3-(trimethylsilyl)-propionate-2,2,3,3-d4 (29Si: 0 ppm) was used as an external standard for the calibration of chemical shifts. Accumulation numbers were fixed at about 10,000.

X-ray photoelectron spectroscopy (XPS) was measured on a VG ESCALAB 220i-XL apparatus at a base pressure of 1 × 10−7 Pa. The X-ray source, voltage, and current were Mg-Kα, 15 kV, and 20 mA, respectively. Binding energies were referenced to those of C 1s (284.8 eV) for 1 and Si 2p (103.4 eV) for 2-5.

Nitrogen adsorption was measured on a Micromeritics ASAP-2020 analyzer (Shimadzu) at 77 K. Each sample (100 mg) was degassed at 373 K for 2 h under vacuum before an adsorption measurement, and the dead volume was estimated by using He.

X-ray absorption fine structure (XAFS) spectra at the Mn K-edge were measured at the BL-9C and BL-12C stations of the Photon Factory at KEK-IMSS. The energy and current of the electrons in the storage ring were 2.5 GeV and 450 mA, respectively. X-rays from the storage ring were monochromatized by Si(111) double crystals. Mn K-edge XAFS of 1 and SiO2-supported Mn catalysts were measured in transmission mode, and ionization chambers filled with pure N2 gas and a mixture of N2 and Ar gases (15/85, v/v) were used to monitor the incident and transmitted X-rays, respectively. Mn catalysts protected by SiO2-matrix overlayers were measured in fluorescence mode, and an ionization chamber filled with N2 and a Lytle detector filled with Ar were used to monitor the incident and fluorescence X-rays, respectively. All samples were measured at 20 K under vacuum. Because of low Mn loading on 5c, Aerosil 300 was also used as a support for the XAFS measurements of 5c.

Mn K-edge XAFS spectra were analyzed with the ATHENA and ARTEMIS programs using the IFEFFIT suite (ver. 1.2.11).29 Mn K-edge XANES spectra were calibrated with Mn foil to the first inflection point of the edge, an energy of 6539.0 eV.30 For Mn K-edge EXAFS analysis, the threshold energy was tentatively set at the first inflection point of the Mn K edge, and background was subtracted by the Autobk method.32 1k-Weighted extended EXAFS oscillations were Fourier transformed into R-space, and single-scattering curve-fitting analysis was performed in R-space with coordination number (CN), interatomic distance (R), Debye–Waller factor (σ2), and correction-of-edge energy (ΔE0) as fitting parameters. Phase shifts and backscattering amplitudes for Mn--Mn and Mn--O(N) were calculated with the FEFF8 code32 from the coordinates of 1 obtained from X-ray single-crystal structural data.26c For the curve fitting of 1, CNs and bond distances were fixed as the average values obtained from X-ray single-crystal structural analysis.

2.6. Catalytic Epoxidation of Alkenes. Each catalyst (Mn4: 0.67 × 10−6 mol) was suspended in a CH2Cl2 solution (3 mL) under 101.3 kPa of O2 in a closed glass reactor equipped with a mechanical stirrer. Alkene epoxidation reactions were conducted at 283 K by the addition of an alkene reactant, biphenyl as an internal standard, and isobutyraldehyde (IBA) to the suspension (Mn4/reactant/biphenyl/IBA = 1/500/250/1500 in molar ratio). To monitor the reaction, reactants and products were analyzed by GC (Shimadzu GC-14B, CHIRALDEX G-TA column) using an internal standard and by GC-MS (Shimadzu GC-2010, CHIRALDEX B-DM column) at appropriate intervals. Inductively coupled plasma (ICP) measurements to estimate Mn amounts in solutions were performed with a plasma spectrometer (SPS 7800, I&I Seiko Instrument Inc.). Activation energy (Ea) was estimated in the temperature range of 283–303 K. After epoxidation of cholesteryl benzoate, the product ratio of α-epoxide/β-epoxide was estimated by 1H NMR.33a

3. RESULTS AND DISCUSSION

3-1. Preparation and Characterization of Supported Mn Clusters on a SiO2 Surface. Chemical grafting of metal complexes allows for easy separation of catalyst from reagents, and prevents the aggregation of metal complexes that lead to deactivation.3,20-22 However, the simple chemical grafting of metal complexes on a support does not always give a stable metal site as catalytically active species, and leaching of the metal species from the surface often proceeds under catalytic reaction conditions.15-19 We have proposed the design of molecularly imprinted metal-complex catalysts on SiO2 surfaces using SiO2-matrix overlayers for imprinting a ligand of a supported metal complex.34 The hydrolysis–polymerization of TMOS deposited on the surface with attached metal complexes can produce surface SiO2-matrix overlayers on the SiO2 surface, whose height can be easily regulated.34 Significant improvements in catalytic performance have been observed on molecularly imprinted metal complex catalysts on SiO2.34
Motivated by these researches, this technique was employed to try to stabilize a Mn cluster supported on the surface of SiO2 particles. The SiO2-supported Mn cluster catalyst was active for epoxidation but easily leached to reaction solutions. The surface of the SiO2 particles with the Mn cluster was functionalized by stacking surface SiO2-matrix overlayers to suppress the leaching of the supported Mn cluster under the reaction conditions. Figure 1 shows schematics of the functionalization of the supported Mn clusters with surface SiO2-matrix overlayers. A MnO2 precursor \([\text{Mn}_4\text{O}_2(\text{CH}_3\text{COO})_7(\text{bipy})_2](\text{ClO}_4)\cdot 3\text{H}_2\text{O}\) (1) was chemically attached on SiO2 particles (Aerosil 200) (2), and subsequently SiO2-matrix overlayers were stacked surrounding the supported Mn cluster by hydrolysis-polymerization of TMOS (5).

The attachment of \([\text{Mn}_4\text{O}_2(\text{CH}_3\text{COO})_7(\text{bipy})_2](\text{ClO}_4)\cdot 3\text{H}_2\text{O}\) (1) onto the surface of SiO2 particles was performed by a wet impregnation method, and one of the CH3COO ligands was observed to be reacted with surface Si–OH groups in the grafting process. Subsequent treatments under vacuum at different temperatures produced different supported Mn clusters (2, 3, and 4), whose structures were characterized by quantitative analysis of CH3COO ligands, FT-IR, DR-UV/vis, and Mn K-edge XAFS. During the impregnation of 1 with SiO2, 0.9 equiv. of CH3COOH to 1 was detected in a CH2Cl2 solution, and a SiO2-attached Mn cluster (2) was obtained. The amount of CH3COO ligands remaining on 2 was observed to be 5.9 equiv. per 1 by a reaction with CF3COOH, which was consistent with the released CH3COOH ligand of 1.

Three broad FT-IR peaks of 2 attributed to \(\nu(\text{CH}_3\text{COOH})_{\text{sym}}\), \(\nu(\text{CH}_3\text{COOH})_{\text{asym}}\) and \(\nu(\text{CH}_3\text{COO})\) of the CH3COO ligands were observed at \(\sim 1420, 1599,\) and \(1345\) cm\(^{-1}\), respectively, which were similar to those of 1 (\(\sim 1404,\) \(\sim 1610,\) and 1336 cm\(^{-1}\)), respectively (Supporting Information, Figure S2 (A)). The shoulders shown on \(\nu(\text{CH}_3\text{COO})_{\text{sym}}\) and \(\nu(\text{CH}_3\text{COO})_{\text{asym}}\) peaks of 2 were lower than 1, suggesting the release of a CH3COO ligand during the attachment. On the other hand, the release of bipy ligands of 1 was not observed during the first impregnation process. Three peaks attributed to the bipy ligands of 2 were observed by FT-IR at 1450, 1472, and 1500 cm\(^{-1}\), which were similar to those of 1 (1448, 1473, and 1499 cm\(^{-1}\)) (Supporting Information, Figure S2 (A)). There was no significant change in the peak intensities of the three peaks attributed to bipy, indicating that the bipy ligands still coordinated to the Mn cluster on 2.

Two peaks attributed to the \(\pi-\pi^*\) transition of the bipy ligands (234 and 294 nm) and two peaks attributed to the \(d-\pi^*\) transition from Mn to the bipy ligands at 442 and 500 nm were observed in the transmittance UV/vis spectrum of 1 in CH2Cl2 (Figure 2). After the attachment of 1 to the SiO2 surface, two characteristic peaks attributed to the \(\pi-\pi^*\) transition of the bipy ligands were still observed at 242 and 303 nm, and two characteristic peaks in the visible region were also observed at 454 and 499 nm. There were no significant changes in the UV/vis region during the first impregnation step.

Edge energy at the Mn K-edge is considered to be relative to the actual oxidation state of Mn species, and the edge energy of the Mn species in 2 was observed to be 6550.4 eV, which was similar to that of 1 (6550.8 eV; Supporting Information, Figure S3, Table S1). The formal oxidation states of four Mn ions were confirmed to be +3 by the ESI-TOF MS spectrum of 1 (Supporting Information, Figure S1). The local coordination structure of 2 was almost similar to that of 1 from Mn K-edge.
EXAFS (vide infra). Therefore, the Mn oxidation state of 2 was suggested to be +3.

The curve-fitting analysis of EXAFS suggested the local coordination structure of the SiO2-supported Mn cluster (2) as shown in Table 1, Figure 3 and Supporting Information, Figure S4. Two peaks of Mn−Mn shown in Table 1, Figure 3 and Supporting Information, Figure S2 was illustrated in Figure 1. The Mn−O−Mn bonds in 1 were negligible in Raman spectroscopy, as is the case in 2.

Table 1. Structural Parameters of 1, 2, 3, and 5c Analyzed by Mn K-edge EXAFS Curve Fitting

<table>
<thead>
<tr>
<th>shell</th>
<th>CN</th>
<th>R  /nm</th>
<th>ΔEw</th>
<th>σ^2/10^6 nm^2</th>
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</thead>
<tbody>
<tr>
<td>1: [Mn4O2(CH3COO)7(C10H8N2)2]ClO4·3H2O^a</td>
<td>Mn−Mn</td>
<td>0.5</td>
<td>0.287 ± 0.001</td>
<td>10 ± 1</td>
</tr>
<tr>
<td>Mn−Mn</td>
<td>2.0</td>
<td>0.335 ± 0.001</td>
<td>10 ± 1</td>
<td>5 ± 1</td>
</tr>
<tr>
<td>Mn−O/N</td>
<td>3.9 ± 0.2</td>
<td>0.191 ± 0.001</td>
<td>8 ± 2</td>
<td>7 ± 1</td>
</tr>
<tr>
<td>Mn−O/N</td>
<td>2.1 ± 0.2</td>
<td>0.219 ± 0.001</td>
<td>8 ± 2</td>
<td>7 ± 1</td>
</tr>
<tr>
<td>2: SiO2-supported Mn cluster (Mn: 2.2 wt %)^b</td>
<td>Mn−Mn</td>
<td>0.8 ± 1.0</td>
<td>0.285 ± 0.010</td>
<td>1 ± 18</td>
</tr>
<tr>
<td>Mn−Mn</td>
<td>1.0</td>
<td>0.335 ± 0.007</td>
<td>14 ± 12</td>
<td>4 ± 8</td>
</tr>
<tr>
<td>Mn−O/N</td>
<td>4.0 ± 2.4</td>
<td>0.189 ± 0.004</td>
<td>4 ± 7</td>
<td>8 ± 4</td>
</tr>
<tr>
<td>Mn−O/N</td>
<td>1.4 ± 2.2</td>
<td>0.220 ± 0.004</td>
<td>4 ± 7</td>
<td>8 ± 4</td>
</tr>
<tr>
<td>3: SiO2-supported Mn cluster (Mn: 2.2 wt %)^b</td>
<td>Mn−Mn</td>
<td>1.3 ± 0.6</td>
<td>0.289 ± 0.003</td>
<td>5 ± 2</td>
</tr>
<tr>
<td>Mn−Mn</td>
<td>0.9 ± 0.5</td>
<td>0.336 ± 0.003</td>
<td>17 ± 5</td>
<td>6 ± 4</td>
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<tr>
<td>Mn−O/N</td>
<td>2.7 ± 0.3</td>
<td>0.187 ± 0.001</td>
<td>3 ± 2</td>
<td>5 ± 1</td>
</tr>
<tr>
<td>5c: SiO2-matrix functionalized Mn cluster (Mn: 0.7 wt %)^c</td>
<td>Mn−Mn</td>
<td>0.7 ± 0.3</td>
<td>0.301 ± 0.008</td>
<td>14 ± 11</td>
</tr>
<tr>
<td>Mn−O/N</td>
<td>1.4 ± 1.7</td>
<td>0.185 ± 0.006</td>
<td>3 ± 9</td>
<td>2 ± 8</td>
</tr>
<tr>
<td>Mn−O</td>
<td>1.0 ± 1.8</td>
<td>0.221 ± 0.013</td>
<td>14 ± 21</td>
<td>2 ± 8</td>
</tr>
</tbody>
</table>

^a k = 30−140 nm⁻¹, R = 0.09−0.34 nm, R_1 = 1.0%. S_0 was fitted to be 0.82. S_1 = 30−120 nm⁻¹, R = 0.08−0.34 nm, R_1 = 0.5%. S_0 = 0.82. S_1R = 30−120 nm⁻¹, R = 0.08−0.34 nm, R_1 = 0.4%. S_0 = 0.82. S_1R = 30−110 nm⁻¹, R = 0.07−0.30 nm, R_1 = 1.6%. S_0 = 0.82.

The UV/vis spectrum of 1 in CH2Cl2 and DR-UV/vis spectra of 2, 3, 4, and 5c in Figure 3. 1, 2, 3, and 5c, measured at 20 K, showed two characteristic peaks in the visible region which were also observed at 454 and 499 nm, suggesting bipy ligands were still coordinated to the Mn center. It might be possible that other similar groups coordinated from the surface to open coordination sites of the Mn cluster.

3-2. Surface Functionalization of SiO2-Matrix Overlayers on the Surface of SiO2 Particles Attaching the Mn Clusters. SiO2-matrix overlayers were prepared on the SiO2-supported Mn clusters (2) by CVD and subsequent hydrolysis-polymerization of tetramethoxysilane (TMOS) and H2O. The stacking procedure and manner of the SiO2-matrix overlayers on SiO2 surfaces so as to surround supported metal complexes have previously been reported.34 We prepared three SiO2-matrix overlayers on 2 to produce three Mn catalysts (5a, 5b, and 5c). The SiO2-matrix overlayers of 5a were prepared by the hydrolysis-polymerization of TMOS in a step...
using 0.67 g of TMOS and 0.27 mL of H2O, respectively (for 0.2 g of 2); that of Sb was prepared using 1.34 g of TMOS and 0.54 mL of H2O (twice amounts of Sa), respectively, in one step CVD/hydrolysis–polymerization process. Sc was prepared by performing the CVD/hydrolysis–polymerization processes twice, using 0.67 g of TMOS and 0.27 mL of H2O, respectively, in each process. In the case of the hydrolysis–polymerization of TMOS for Sa, almost 70% of the used TMOS was actually polymerized under the conditions.

Figure 4(A) shows $^{29}$Si solid-state MAS NMR spectra of Sa, Sb, and Sc with SiO2-matrix overlayers, and three Si components of Q4 (Si(OSi)$_4$), Q3 (Si(OSi)$_3$(OH)), and Q2 (Si(OSi)$_2$(OH)$_2$) at around −111, −102, and −92 ppm, respectively, were observed. Difference between the spectra of S and 2 is attributed to Si species of the SiO2-matrix overlayers of S, and the sum of areas of three Q$_n$ Q$_2$ and Q$_2$ peaks in a difference spectrum (S − 2) is relative to the amount of stacked Si species by the hydrolysis–polymerization (Supporting Information, Figure S5). Although there is a possibility that the quantitative peak analyses of $^{29}$Si NMR spectra might be affected by paramagnetic Mn cluster complex (some Si sites might not be observed by $^{29}$Si NMR), the effect of paramagnetic species was considered to be not significant in the current case since NMR of Mn$_{4}$ cluster (1) was measurable. The ratio of the sum of the peak areas of SiO2-matrix overlayers on Sa, Sb, and Sc was estimated to be 1/1.1/2.2. It was found that the repetition of the hydrolysis–polymerization cycles was efficient to increase the amount of SiO2-matrix overlayers (Sc), while the simple increase in the amounts of used TMOS and H2O for the hydrolysis–polymerization process was inefficient (Sb).

When 70% of used TMOS was polycondensed, the Si atomic ratio of the SiO2-matrix overlayers to the SiO2 support was 0.92. The Si atomic ratio calculated by using the peak intensities (the summation of the peak intensities of the three Si species) of $^{29}$Si NMR in Figure 4A was 0.93, which agreed with the value calculated for mass gain. Assuming that the SiO2-matrix overlayers spread on the surface of the SiO2 support were of quartz structure, which exhibits the largest density of SiO2, the calculated height of the observed amount of the SiO2-matrix overlayers on Sa was 2.2 nm on the used SiO2 support (Aerosil 200; surface area: 200 m$^2$ g$^{-1}$). In the case of Sc, the calculated height of the SiO2-matrix overlayers was 4.3 nm. The average particle size of the SiO2 support (Aerosil 200) was as small as 12 nm and each SiO2 particles gathered each other. It was difficult to estimate the actual average heights of the SiO2-matrix overlayers by TEM. Transmission electron microscopy (TEM) revealed the morphological differences of 2 and Sc (Figure 1(B) and Supporting Information, Figure S6). The surface of Sc with the SiO2-matrix overlayers was rougher after the stacking of SiO2-matrix overlayers than that of 2, and surface thin layers were observed as shown in Figure 1(B).

The ratios of the three Si species on Sc were estimated to be 4% (Q$_4$), 34% (Q$_3$), and 62% (Q$_2$), respectively (Supporting Information, Figure SS). The major species being Q$_4$ indicated that Si–O–Si networks were formed by the hydrolysis–polymerization of TMOS. On the other hand, the Si species on Sb were 10% (Q$_4$), 42% (Q$_3$), and 48% (Q$_2$), respectively. The amount of TMOS used for the hydrolysis-polymerization affected not only the amount of stacked SiO2 matrix but also the ratio of these compositions.

Significant differences were also observed in the surface areas of 2, Sa, Sb, and Sc. N$_2$ adsorption isotherms at 77 K and their t-plots are presented in Supporting Information, Figure S7. The N$_2$ adsorption/desorption isotherms suggest increases in surface areas after the stacking of the SiO2-matrix overlayers as well as the formation of micropores in the matrix overlayers. Brunauer–Emmett–Teller (BET) surface areas and external surface areas were respectively estimated to be 182 and 164 m$^2$ g$^{-1}$ for 2, 347 and 286 m$^2$ g$^{-1}$ for Sa, 578 and 529 m$^2$ g$^{-1}$ for Sb, and 294 and 197 m$^2$ g$^{-1}$ for Sc. Note that the external surface area of Sc was similar to that of 2, while the external surface areas of Sa and Sb were relatively higher than that of 2. These results implied that the hydrolysis–polymerization produced a SiO2 matrix with micropores and that repetition of the process tended to fill up the rough structures of the SiO2 matrix, retaining the external surface area of the SiO2 particles. The t-plot of Sc had a gentle break at 0.37 nm, suggesting the formation of micropores with an average diameter of 0.74 nm.

Figure 4(B) shows Mn 2p$_3/2$ and 2p$_1/2$ XPS spectra of 2, Sa, Sb, and Sc. Mn 2p$_3/2$ and 2p$_1/2$ peaks for 1 were clearly observed at 641.7 and 653.4 eV, respectively, and those for 2 on SiO2 were observed at 642.2 and 653.9 eV, respectively. The slight shifts in the Mn 2p binding energies would reflect the coordination of surface oxygen to the Mn complex. After the stacking of the SiO2-matrix overlayers, the Mn 2p peaks were observed to get smaller. Even the Mn 2p peaks of Sa entirely disappeared, as did those of Sb and Sc (Figure 4(B)). Considering the escape depth of Mn 2p, these results clearly indicated that the supported Mn clusters on the surface of the SiO2 particles were closely surrounded by the produced SiO2-matrix overlayers.

It was found out that the structure of Sc after stacking of the SiO2-matrix overlayers was different from that of 2. Mn K-edge EXAFS found the local coordination structure of the supported Mn species on Sc: Mn···Mn interaction length of 0.301 ± 0.008 nm (CN = 1.0 ± 0.1) and two Mn···O interactions at 0.185 ± 0.006 nm (CN = 1.0 ± 0.1) (Table 1, Figure 3 and Supporting Information, Figure S4). The amount of remaining CH$_3$COO ligands of Sc was estimated to be 2.0 equiv to Mn$_{4}$ in the DR-UV/vis spectrum of Sc, the characteristic peaks attributed to $\pi$-$\pi'$ transition from Mn to the bipy ligands disappeared (Figure 2(B)). These results indicated that the partial release of the coordinating ligands brought about the transformation of the supported Mn cluster to dimeric Mn species in the SiO2-matrix overlayers. Therefore, a possible composition of dimeric Mn species on Sc...
could be written as \([\text{Mn}_2(\text{CH}_3\text{COO})_2]_2\), although the exact detailed structure was still controversial at this moment. The edge energy obtained from Mn K-edge XANES in 5c (6548.7 eV; Supporting Information, Figure S3, Table S1) was smaller than that in 2, suggesting the reduction of the Mn species.

### 3-3. Catalytic Performance in Alkene Epoxidation

Alkene epoxidation using O₂ and IBA (a sacrificial reagent) was examined on the supported Mn clusters (2−4 and 5a−c). The results are summarized in Table 2. The homogeneous solution of 1 promoted the epoxidation of trans-stilbene with high selectivity of 94% (entry 3), whereas no reaction occurred without 1 (entry 1). The SiO₂-supported Mn clusters, 2−4, showed activity and high selectivity over 95% (entries 4−6), whereas SiO₂ without Mn was inactive (entry 2). After a reaction was completed, the solid catalysts were separated from the solution phases, and the amounts of leached Mn species were determined by ICP measurements. It was found out that the leaching of the supported Mn complexes was substantial: 45.8% for 2, 53.4% for 3, and 47.3% for 4. These results suggested that these supported Mn clusters that were simply attached to the surface were not durable under heterogeneous epoxidation conditions.

The preparation of the SiO₂-matrix overlays on the SiO₂-supported Mn clusters imparted the catalyst with remarkable stability (Table 2). The supported Mn catalysts with the SiO₂-matrix overlays (5a, 5b, and 5c) promoted the epoxidation with high selectivity for trans-stilbene epoxide: 91% for 5a, 88% for 5b, and 91% for 5c at ~90% conversion for 24−33 h (entries 7−9). Although the epoxidation reaction became slower, the leaching of the active Mn catalyst was significantly suppressed on 5a−c. The amounts of leached Mn species were 0.41% for 5a and negligible for 5b (0.02%) and 5c (0.01%). When the reaction was run to a conversion of ~50%, the reaction solution was filtered from solid 5c and showed no further progress in the catalytic reaction (Figure 5(A)). On the other hand, the filtration of 3 was significantly active. These results clearly show that the supported Mn catalysts embedded in the SiO₂-matrix overlayers, in particular 5c, were highly stable, and that the catalytic reaction on 5c proceeded in the heterogeneous phase without unfavorable leaching of Mn into solution. In contrast, dissolved Mn in the solution was active on 3. After the 500 cycle of epoxidation, no Mn−Mn interaction was observed on 5c (Supporting Information, Figure S4 and Table S2). The decrease in the amount of Mn in the catalyst was not observed during the reaction, suggesting that transient leaching and re-deposition of the Mn species would not contribute to the reaction.

Figures 5(B), 5(C), and Supporting Information, Figure S8 show the conversion of trans-stilbene, the selectivity of trans-stilbene oxide, and the amount of Mn species remaining on the SiO₂ particle surface on the catalysts 3 and 5c after they were recycled 5 times. On 3 without the SiO₂-matrix overlayers, the conversion decreased significantly because of the extensive leaching of Mn species into solution. After 2 cycles of
observed major byproducts were aldehydes from 3ff conversion of overlayers was negligible after 6 epoxidation cycles, and the epoxidation of cholesteryl benzoate provides two epoxide Mn epoxidation catalysts. 5c byproducts. selectivity, whereas the selectivity of terminal alkene such as 1-position. The reactions of internal alkenes such as cyclohexene, trans leaching of the Mn catalyst on surface SiO2-matrix overlayers on the stability of the supported Mn clusters were lost (Supporting Information, Figure S8). On the other hand, the epoxidation, 80% of the supported Mn clusters were lost (for 30 h) in trans-stilbene epoxidation. (B) Conversion of each cycle; (C) selectivity for epoxide; reaction conditions: Mn4, 0.67 −

We also investigated the epoxidation of cholesteryl benzoate using m-chloroperbenzoic acid (m-CPBA) and the Mn catalyst 5c. The experiment suggests whether a Mn center contributes to the oxidation step in epoxidation cycle or not. 53a The epoxidation of cholesteryl benzoate provides two epoxide products, α-epoxide and β-epoxide (Scheme 1). In the case of autoxidation using peroxy species (e.g., m-CPBA), α-epoxide is preferably produced. Analogously, if a free peroxy species were to be formed on the Mn site, but reacted independently with an alkene reactant in solution (in a similar way as autoxidation), the selective formation of α-epoxide would also be observed. On the other hand, if the epoxidation step were to proceed on a metal surface, the steric hindrance between the cholesteryl benzoate at 5 and 6-position and the metal center is expected to change the selectivity of the products. It was reported that the selectivity of the cholesteryl benzoate epoxidation changed (β-epoxide was preferably obtained) when catalytic amounts of Mn(II) complexes were used in the O2/IBA system. For instance, the α-epoxide/β-epoxide product ratio on bis(acyclacetono)manganese(II) was reported to be 20/80 and that on bis(dipivaloylmethanato)manganese(II) was 18/82. 33a

We performed the epoxidation of the cholesteryl benzoate with m-CPBA and 5c. With m-CPBA without the Mn catalysts, the α-epoxide was preferably formed with the α-epoxide/β-epoxide product ratio of 73/27 (6.5 h; determined by 1H NMR), which agreed with reported results. On the other hand, the product ratio of α-epoxide/β-epoxide was 20/80 (24 h) on 5c. The reaction mechanism and intermediate structures on 5c are not clear at the moment, but the opposite epoxide selectivity for the epoxidation of the cholesteryl benzoate suggests that the Mn species on 5c surrounded by the SiO2-matrix overlayers indeed are involved in the epoxidation step. It is to be noted that the activation energy of catalytic epoxidation on 5c differed widely by alkene. Cyclooctene epoxidation had similar activation energies on 3 (15 kJ mol−1) and 5c (16 kJ mol−1), and the turnover frequencies (TOFs) were 4.0 × 10−2 and 1.9 × 10−2 s−1, respectively. On the other hand, the TOFs and activation energies for the epoxidation of the larger reactant trans-stilbene on 5c were 6.7 × 10−3 s−1 and 31 kJ mol−1, whereas those on 3 were 2.5 × 10−3 s−1 and 15 kJ mol−1. The small activation energies around 15 kJ mol−1 on 3 might be related to mass transfer. The smaller reaction rate of trans-stilbene on 5c is due to the diffusion resistance of the reactants inside the SiO2-matrix overlayers. The 2-fold higher activation energies for the trans-stilbene epoxidation on 5c would result from the different transition state structure produced from the reactant, the oxidant, and the Mn species on 5c inside the SiO2-matrix overlayers. Since the structure of Mn species on 5c was totally different from that on 3, the loss of CH3COO and bipy ligands, the addition of surface silanol groups, and the existence of SiO2-matrix overlayers, the structures of transition state and intermediate responsible for determining activation energy would be different. The steric hindrance for the coordination and subsequent oxidation of trans-stilbene at the Mn site inside the surface-matrix overlayers would also be one of the reasons to produce the different transition state/intermediate structures. 34a Similar trends were observed for the cholesteryl benzoate epoxidation (14 kJ mol−1 on 3; 74 kJ mol−1 on 5c), supporting the above discussion.
We also prepared catalyst 6 by releasing the ligands of 2 at 673 K so that 6 had MnO₃ as supported species. Catalyst 7 was prepared by subsequent stacking of SiO₂-matrix overlayers on 6 with MnO₂ species. It is to be noted that 6 and 7 exhibited different epoxidation performances as shown in Table 2. Catalyst 6 exhibited a similar behavior to catalysts 2, 3, and 4 (conversion: 99%, epoxide selectivity: 97%) for the trans-stilbene epoxidation, and significant leaching was observed (38.6% for 12 h) (entry 12). On the contrary, the epoxidation was suppressed on 7, and the corresponding epoxide was not observed even after 36 h (entry 13). These results suggested that the stacking of the SiO₂-matrix overlayers on the MnO₃ species without the coordinating ligands did not provide reaction space above the Mn site, resulting in large loss of the catalytic activity.

Although the coordination structure of 5c decomposed from the Mn₄ clusters (1 and 2) during the preparation step of the SiO₂-matrix overlayers, the catalyst 5c prepared on 2 with the Mn cluster with the several coordinating ligands cannot be obtained from the simple supported MnO₃ species on the SiO₂ surface. Indeed, 5c, whose complete local coordination structure is not clear at the moment, exhibited robust epoxidation performances under the identical conditions. The integration of the active Mn site and the surface SiO₂-matrix overlayers would cooperatively achieve robust catalysis in the heterogeneous phase.

4. CONCLUSIONS

The functionalization of the surface of SiO₂ particles with attached [Mn₃O₂(CH₃COO)₃(bipy)₃]ClO₄·3H₂O (1) and the stacking of SiO₂-matrix overlayers were successfully used to prepare a new and robust heterogeneous Mn catalyst for the selective epoxidation of alkenes. 1 was chemically attached to a SiO₂ particle surface, and the attached structure was characterized by FT-IR, UV/vis, Raman spectroscopy, XPS, and Mn K-edge XAFS. The stacking of surface SiO₂-matrix overlayers surrounding the supported Mn clusters of 2 with a similar structure to the precursor 1 brought about a structural change in the original Mn cluster to an active dimeric Mn species on 5c together with the formation of a reaction space in the close proximity of the Mn species inside the SiO₂-matrix overlayers. 5c exhibited different catalytic activity, especially in the reaction rate and activation energy compared with 2 and 3, and the durability of the Mn catalysts under the epoxidation reaction conditions was remarkably improved. The leaching of the supported Mn catalysts on 5c was prevented. The surface functionalization through the SiO₂-matrix overlayers to provide the composite of an active metal site and a reaction space is promising to achieve a robust catalysis on a supported metal catalyst in a heterogeneous phase.

ASSOCIATED CONTENT

Supporting Information
An ESI-TOM MS spectrum, FT-IR spectra, Mn K-edge XANES and EXAFS spectra and their analyses, ²⁹Si NMR spectra, N₂ adsorption, TEM images, and residual Mn ratio in recycling tests. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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