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

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 Ⓢ *Supporting Information*
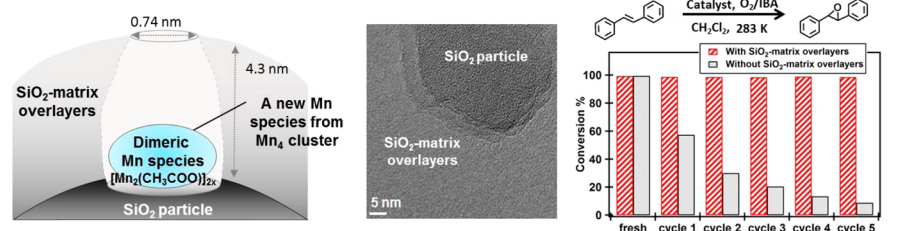
ABSTRACT: A robust heterogeneous Mn catalyst for selective epoxidation was prepared by the attachment of a Mn_4 oxonuclear complex $[Mn_4O_2(CH_3COO)_7(bipy)_2](ClO_4) \cdot 3H_2O$ (**1**) on SiO_2 and the successive stacking of SiO_2-matrix overlayers around a supported Mn cluster. The structures of 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 CH_3COO ligand of **1** and surface silanol group produced a SiO_2-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 CH_3COO 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 epoxid, 96%, for 6 h on **3**). We found that the functionalization of the supported Mn cluster on **2** with surface SiO_2-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 SiO_2-matrix overlayers. By optimizing the stacking manner of the SiO_2-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, SiO_2 particles, surface functionalization, SiO_2-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.

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-trimethylcyclononane (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 O_2 and H_2O_2. Mn oxonuclear clusters with acetate and phosphate ligands have attracted considerable attention because they were potential models of metal enzyme active sites,[4b,8] such as catalase[9] and the water oxidation center in Photosystem II.[10] The activity for oxidation of alcohols,[11] epoxidation and *cis*-dihydroxylation of alkenes,[7h−j,11b,12] sulfoxidation,[11b,13] and oxidation of alkanes[11b,14] 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 SiO_2,[16] clays,[17] zinc−aluminum double hydroxides,[18] 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 SiO_2 surface toward robust epoxidation catalysis in a heterogeneous phase. A Mn oxotetranuclear cluster, $[Mn_4O_2(CH_3COO)_7(bipy)_2](ClO_4) \cdot 3H_2O$ (1),[26a] which has been prepared as a series of model complexes for Photosystem II,[26,27] was chemically attached on the surface of SiO_2 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 SiO_2 surface by stacking SiO_2-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 SiO_2 surface, and the robust epoxidation performances were achieved on the Mn catalyst in a heterogeneous phase.

2. EXPERIMENTAL SECTION

2-1. Preparation of $[Mn_4O_2(CH_3COO)_7(bipy)_2](ClO_4) \cdot 3H_2O$ (1).
All reagents were purchased from Sigma-Aldrich, STREM, Wako Chemicals, and Tokyo Kasei Kogyo, and used as received unless otherwise noted. $[Mn_3O(CH_3COO)_6(py)_3](ClO_4)$ was prepared by the literature method[28] and $[Mn_4O_2(CH_3COO)_7(bipy)_2](ClO_4) \cdot 3H_2O$ (1) was synthesized by literature reported procedure with modifications.[26a]

Under N_2 atmosphere, 2,2′-bipyridine (bipy) (1.15 g, 7.36 mmol) was added to a stirred MeCN solution (50 mL) of $[Mn_3O(CH_3COO)_6(py)_3](ClO_4)$ (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 Et_2O (50 mL) and additional Et_2O (20 mL). The powder was collected by filtration, washed with Et_2O, and dried; yield 70.9% (from Mn basis). Compound 1 was obtained as a dark red powder in trihydrate form. Anal. Calcd for $C_{34}H_{43}N_4O_{23}ClMn_4$: C, 36.11; H, 3.83; N, 4.95;. Found: C, 36.29; H, 3.65; N, 5.14. ^1H NMR (CD_2Cl_2): −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 (CH_2Cl_2): m/z 976.9320 $[M]^+$ (Calcd for $C_{34}H_{37}O_{16}N_4Mn_4$, 976.9727) (Supporting Information, Figure S1).

2-2. Preparation of SiO_2-Supported Mn_4 Cluster (2).
SiO_2 (1 g, Aerosil 200, Degussa, surface area: 200 m^2 g^{-1}) was calcined at 673 K for 2 h and kept under vacuum for 0.5 h prior to the grafting of 1. The precalcined SiO_2 (1 g) was suspended in CH_2Cl_2 (20 mL) under N_2, and a CH_2Cl_2 solution (10 mL) of 1 (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 SiO_2-Matrix Overlayers.
A SiO_2 matrix protecting Mn catalyst (5a) was prepared as follows. Tetramethoxysilane (TMOS, $Si(OCH_3)_4$) (0.67 g (0.65 mL)) and distilled H_2O (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 H_2O 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 SiO_2 matrix (5b) was prepared in a similar way with double the amounts of TMOS (1.34 g) and H_2O (0.54 mL). A Mn catalyst protected by a SiO_2 matrix (5c) was prepared by twice performing the procedure of stacking SiO_2-matrix overlayers of TMOS (0.67 g) and H_2O (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 SiO$_2$-Supported MnO$_x$ Catalysts. 2 was heated for 3 h at 673 K under vacuum to prepare catalyst **6**. Catalyst **7** was prepared by the stacking of SiO$_2$-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 $K\alpha$ and Si $K\alpha$. The amount of CH$_3$COO ligands released from Mn clusters during the attachment to SiO$_2$ was determined as follows. After the impregnation of SiO$_2$ with **1** in a Schlenk tube under N$_2$ atmosphere, the resulting supernatant was decanted from the suspension, and the released CH$_3$COOH was dissolved and quantified by gas chromatography using a flame ionization detector (FID-GC; Shimadzu GC-14B, CHIRAL-DEX B-DM column). The number of CH$_3$COO ligands in **2**, **3**, **4**, and **5c** were determined as follows. The catalysts were treated with excess amount of CF$_3$COOH in CH$_2$Cl$_2$ solution, and the removed CH$_3$COOH 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 Mn$_4$ 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**, and **4** were measured under in situ conditions using a neat disk of **2** prepared under N$_2$ 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 **4** 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 CH$_2$Cl$_2$. Solid **2**, **3**, **4**, and **5** were placed in quartz cells under Ar atmosphere.

^{29}Si solid-state magic angle spinning (MAS) NMR spectra were recorded with a JEOL JNM-ECX400 spectrometer operating at 79.5 MHz. A single-pulse detection method was used in ^{29}Si 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,-d_4 (^{29}Si: 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-$K\alpha$, 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 SiO$_2$-supported Mn catalysts were measured in transmission mode, and ionization chambers filled with pure N$_2$ gas and a mixture of N$_2$ and Ar gases (15/85, v/v) were used to monitor the incident and transmitted X-rays, respectively. Mn catalysts

protected by SiO$_2$-matrix overlayers were measured in fluorescence mode, and an ionization chamber filled with N$_2$ 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.[29a,31] k^3-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 (σ^2), and correction-of-edge energy (ΔE_0) as fitting parameters. Phase shifts and backscattering amplitudes for Mn···Mn and Mn−O(N) were calculated with the FEFF8 code[32] 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 CH$_2$Cl$_2$ solution (3 mL) under 101.3 kPa of O$_2$ 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 (Mn$_4$/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, SII Seiko Instrument Inc.). Activation energy (E_a) 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 ^{1}H NMR.[33a]

3. RESULTS AND DISCUSSION

3-1. Preparation and Characterization of Supported Mn Clusters on a SiO$_2$ 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 SiO$_2$ surfaces using SiO$_2$-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 SiO$_2$-matrix overlayers on the SiO$_2$ surface, whose height can be easily regulated.[34] Significant improvements in catalytic performance have been observed on molecularly imprinted metal complex catalysts on SiO$_2$.[34]
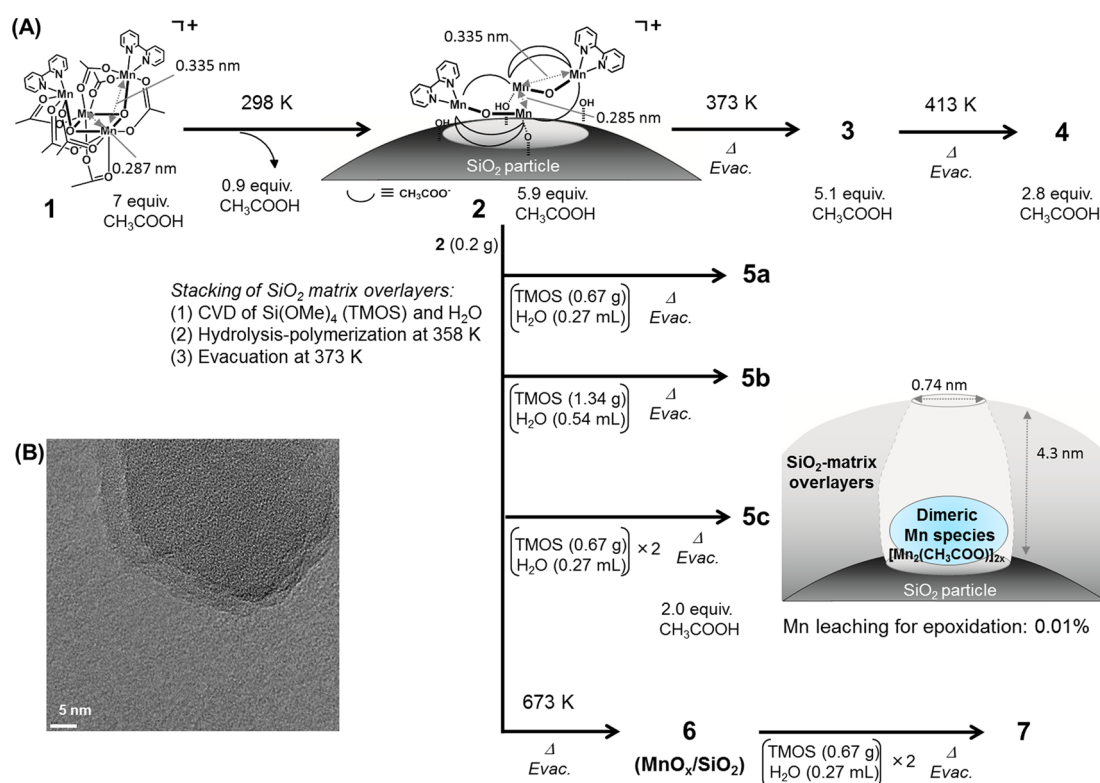
Figure 1. (A) Schematics of the attachment of the Mn_4O_2 cluster (**1**) on the surface of SiO_2 and surface functionalization with SiO_2-matrix overlayers to produce nanopores protecting the supported Mn cluster. (B) HRTEM images of a SiO_2 particle of **5c** with the SiO_2 matrix. The average particle size of Aerosil 200 support was 12 nm (reported by the product company), but it was difficult to visualize SiO_2 overlayers on such small particles, which gathered each other.

Motivated by these researches, this technique was employed to try to stabilize a Mn cluster supported on the surface of SiO_2 particles. The SiO_2-supported Mn cluster catalyst was active for epoxidation but easily leached to reaction solutions. The surface of the SiO_2 particles with the Mn cluster was functionalized by stacking surface SiO_2-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 SiO_2-matrix overlayers. A Mn_4O_2 precursor $[Mn_4O_2(CH_3COO)_7(bipy)_2](ClO_4)\cdot 3H_2O$ (**1**) was chemically attached on SiO_2 particles (Aerosil 200) (**2**), and subsequently SiO_2-matrix overlayers were stacked surrounding the supported Mn cluster by hydrolysis-polymerization of TMOS (**5**).

The attachment of $[Mn_4O_2(CH_3COO)_7(bipy)_2](ClO_4)\cdot 3H_2O$ (**1**) onto the surface of SiO_2 particles was performed by a wet impregnation method, and one of the CH_3COO 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 CH_3COO ligands, FT-IR, DR-UV/vis, and Mn K-edge XAFS. During the impregnation of **1** with SiO_2, 0.9 equiv. of CH_3COOH to **1** was detected in a CH_2Cl_2 solution, and a SiO_2-attached Mn cluster (**2**) was obtained. The amount of CH_3COO ligands remaining on **2** was observed to be 5.9 equiv. per **1** by a reaction with CF_3COOH, which was consistent with the released CH_3COOH ligand of **1**.

Three broad FT-IR peaks of **2** attributed to $\nu(CH_3COO)_{sym}$, $\nu(CH_3COO)_{asym}$, and $\nu(CH_3COO)$ of the CH_3COO ligands were observed at ~1420, 1599, and 1345 cm^{-1}, respectively,

which were similar to those of **1** (~1404, ~1610, and 1336 cm^{-1}, respectively) (Supporting Information, Figure S2 (A)). The shoulders shown on $\nu(CH_3COO)_{sym}$ and $\nu(CH_3COO)_{asym}$ peaks of **2** were lower than **1**, suggesting the release of a CH_3COO 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-π^* transition from Mn to the bipy ligands at 442 and 500 nm were observed in the transmittance UV/vis spectrum of **1** in CH_2Cl_2 (Figure 2). After the attachment of **1** to the SiO_2 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
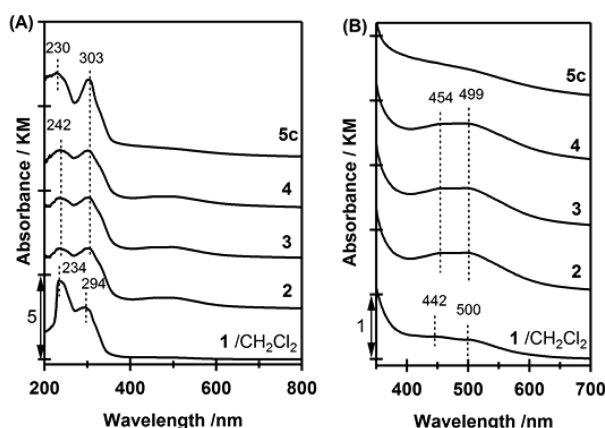
Figure 2. (A) UV/vis spectrum of **1** in CH_2Cl_2 and DR-UV/vis spectra of **2**, **3**, **4**, and **5c**. (B) Magnified view from 350 to 700 nm.

Figure 3. k^3-Weighted Mn K-edge EXAFS Fourier transforms for **1**, **2**, **3**, and **5c**, measured at 20 K.

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 SiO_2-supported Mn cluster (**2**) as shown in Table 1, Figure 3 and Supporting Information, Figure

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

shell	CN	R /nm	ΔE_0	$\sigma^2/10^5$ nm²
1: $[Mn_4O_2(CH_3COO)_7(C_{10}H_8N_2)_2]ClO_4 \cdot 3H_2O^a$				
Mn···Mn	0.5	0.287 ± 0.001	10 ± 1	2 ± 1
Mn···Mn	2	0.335 ± 0.001	10 ± 1	5 ± 1
Mn−O/N	3.9 ± 0.2	0.191 ± 0.001	8 ± 2	7 ± 1
Mn−O/N	2.1 ± 0.2	0.219 ± 0.001	8 ± 2	7 ± 1
2: SiO_2-supported Mn cluster (Mn: 2.2 wt %)^b				
Mn···Mn	0.8 ± 1.0	0.285 ± 0.010	1 ± 18	5 ± 8
Mn···Mn	1.0 ± 1.2	0.335 ± 0.007	14 ± 12	4 ± 8
Mn−O/N	4.0 ± 2.4	0.189 ± 0.004	4 ± 7	8 ± 4
Mn−O/N	1.4 ± 2.4	0.220 ± 0.004	4 ± 7	8 ± 4
3: SiO_2-supported Mn cluster (Mn: 2.2 wt %)^c				
Mn···Mn	1.3 ± 0.6	0.289 ± 0.003	5 ± 4	9 ± 4
Mn···Mn	0.9 ± 0.5	0.336 ± 0.003	17 ± 5	6 ± 4
Mn−O/N	2.7 ± 0.3	0.187 ± 0.001	3 ± 2	5 ± 1
5c: SiO_2-matrix functionalized Mn cluster (Mn: 0.7 wt %)^d				
Mn···Mn	0.7 ± 0.3	0.301 ± 0.008	14 ± 11	9
Mn−O	1.4 ± 1.7	0.185 ± 0.006	3 ± 9	2 ± 8
Mn−O	1.0 ± 1.8	0.221 ± 0.013	14 ± 21	2 ± 8

$^a k = 30-140$ nm^{-1}, $R = 0.09-0.34$ nm, $R_f = 1.0\%$. S_0 was fitted to be 0.82. $^b k = 30-120$ nm^{-1}, $R = 0.08-0.34$ nm, $R_f = 0.5\%$. $S_0 = 0.82$. $^c k = 30-120$ nm^{-1}, $R = 0.08-0.34$ nm, $R_f = 0.4\%$. $S_0 = 0.82$. $^d k = 30-110$ nm^{-1}, $R = 0.07-0.30$ nm, $R_f = 1.6\%$. $S_0 = 0.82$.

S4. Two peaks of Mn···Mn at 0.285 and 0.335 nm were observed on **2**. The contribution of the long Mn···Mn interaction decreased to half, while the short Mn···Mn interaction remained: two Mn···Mn interactions at 0.285 ± 0.010 nm (coordination number (CN) = 0.8 ± 1.0) and at 0.335 ± 0.007 nm (CN = 1.0 ± 1.2) were fitted, together with Mn−O(N) at 0.189 ± 0.004 nm (CN = 4.0 ± 2.4) and 0.220 ± 0.004 nm (CN = 1.4 ± 2.4). Similar UV/vis and Mn K-edge XANES spectra of **1** and **2** indicated that the coordination structure of the Mn cluster of **2** was similar to that of **1**. However, the structural parameters obtained by Mn K-edge EXAFS suggested that two Mn atoms at the edge position of
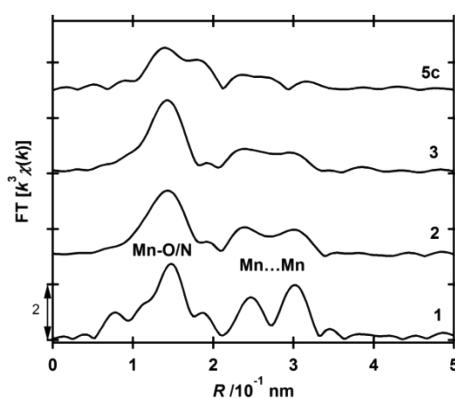
the Mn_4 butterfly framework of **1** stuck out, leading to the distortion of the Mn_4 cluster framework with the decrease in the CN of the long Mn−Mn interaction at 0.335 nm. A possible model of **2** is illustrated in Figure 1. The Mn−O−Mn bonds in **1** were negligible in Raman spectroscopy, as is the case in **2**.

We investigated further the treatment of **2** under vacuum at different temperatures to release extra CH_3COO ligands from the supported Mn complex. When **2** was heated at 373 K, in situ FT-IR measurements suggested that one of the six CH_3COO ligands on **2** was released, and the peak intensities attributed to the CH_3COO ligands remaining in **3** further decreased (Supporting Information, Figure S2(B)). The amount of CH_3COO ligands on **3** was estimated by GC to be 5.1 equiv relative to Mn_4. Further treatment under vacuum at 413 K produced **4** with 2.8 equiv of CH_3COO ligands relative to Mn_4. Mn K-edge XANES and EXAFS revealed that the Mn K-edge energy in **3** was similar to that in **2** (6550.5 eV; Supporting Information, Figure S3, Table S1); however, the CN of the Mn−O(N) interaction became smaller than that of **2** (Table 1). The edge energy suggested that the Mn oxidation state of **3** is +3. However, edge energy varies (~2 eV) when the coordination structures of metal complexes and the type of ligands are different even if they have the same formal oxidation states,[35] and it is difficult to conclude the details of the coordination structure of **3** from the obtained parameters from the curve-fitting analysis of EXAFS. The obvious fact is that bridging CH_3COO ligands were partially released by the heat treatment at 373 K (**3**), and the trend was enhanced at 413 K (**4**). DR-UV/vis spectra of **3** and **4** (Figure 2) 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 silanol groups coordinated from the surface to open coordination sites of the Mn cluster.

3-2. Surface Functionalization of SiO_2-Matrix Overlayers on the Surface of SiO_2 Particles Attaching the Mn Clusters. SiO_2-matrix overlayers were prepared on the SiO_2-supported Mn clusters (**2**) by CVD and subsequent hydrolysis−polymerization of tetramethoxysilane (TMOS) and H_2O. The stacking procedure and manner of the SiO_2-matrix overlayers on SiO_2 surfaces so as to surround supported metal complexes have previously been reported.[34] We prepared three SiO_2-matrix overlayers on **2** to produce three Mn catalysts (**5a**, **5b**, and **5c**). The SiO_2-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 H_2O, respectively (for 0.2 g of **2**); that of **5b** was prepared using 1.34 g of TMOS and 0.54 mL of H_2O (twice amounts of **5a**), respectively, in one step CVD/hydrolysis−polymerization process. **5c** was prepared by performing the CVD/hydrolysis−polymerization processes twice, using 0.67 g of TMOS and 0.27 mL of H_2O, respectively, in each process. In the case of the hydrolysis−polymerization of TMOS for **5a**, almost 70% of the used TMOS was actually polymerized under the conditions.

Figure 4(A) shows ^{29}Si solid-state MAS NMR spectra of **5a**, **5b**, and **5c** with SiO_2-matrix overlayers, and three Si
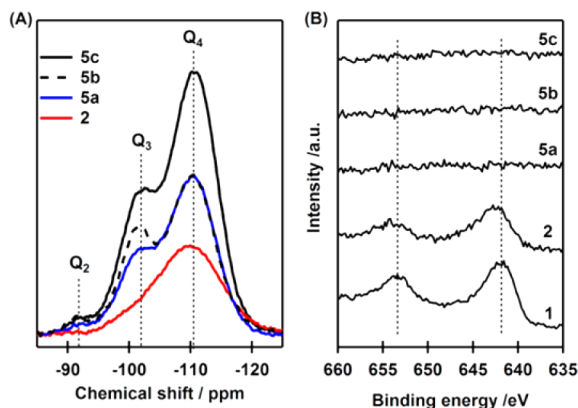

Figure 4. (A) ^{29}Si solid-state MAS NMR of **2**, **5a**, **5b**, and **5c**, and (B) Mn 2p XPS spectra of **1**, **2**, **5a**, **5b**, and **5c**.

components of Q_4 ($Si(OSi)_4$), Q_3 ($Si(OSi)_3(OH)$), and Q_2 ($Si(OSi)_2(OH)_2$) at around −111, −102, and −92 ppm, respectively, were observed. Difference between the spectra of **5** and **2** is attributed to Si species of the SiO_2-matrix overlayers of **5**, and the sum of areas of three Q_4, Q_3, and Q_2 peaks in a difference spectrum (**5** − **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 area 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 SiO_2-matrix overlayers on **5a**, **5b**, and **5c** 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 SiO_2-matrix overlayers (**5c**), while the simple increase in the amounts of used TMOS and H_2O for the hydrolysis-polymerization process was inefficient (**5b**).

When 70% of used TMOS was polycondensed, the Si atomic ratio of the SiO_2-matrix overlayers to the SiO_2 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 SiO_2-matrix overlayers spread on the surface of the SiO_2 support were of quartz structure, which exhibits the largest density of SiO_2, the calculated height of the observed amount of the SiO_2-matrix overlayers on **5a** was 2.2 nm on the used SiO_2 support (Aerosil 200; surface area: 200 m^2 g^{-1}). In the case of **5c**, the calculated height of the SiO_2-matrix overlayers was 4.3 nm. The average particle size of the SiO_2 support (Aerosil 200) was as

small as 12 nm and each SiO_2 particles gathered each other. It was difficult to estimate the actual average heights of the SiO_2-matrix overlayers by TEM. Transmission electron microscopy (TEM) revealed the morphological differences of **2** and **5c** (Figure 1(B) and Supporting Information, Figure S6). The surface of **5c** with the SiO_2-matrix overlayers was rougher after the stacking of SiO_2-matrix overlayers than that of **2**, and surface thin layers were observed as shown in Figure 1(B).
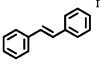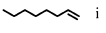
The ratios of the three Si species on **5c** were estimated to be 4% (Q_2), 34% (Q_3), and 62% (Q_4), respectively (Supporting Information, Figure S5). The major species being Q_4 indicated that Si−O−Si networks were formed by the hydrolysis−polymerization of TMOS. On the other hand, the Si species on **5b** were 10% (Q_2), 42% (Q_3), and 48% (Q_4), respectively. The amount of TMOS used for the hydrolysis-polymerization affected not only the amount of stacked SiO_2 matrix but also the ratio of these compositions.

Significant differences were also observed in the surface areas of **2**, **5a**, **5b**, and **5c**. 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 SiO_2-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 **5a**, 578 and 529 m^2 g^{-1} for **5b**, and 294 and 197 m^2 g^{-1} for **5c**. Note that the external surface area of **5c** was similar to that of **2**, while the external surface areas of **5a** and **5b** were relatively higher than that of **2**. These results implied that the hydrolysis−polymerization produced a SiO_2 matrix with micropores and that repetition of the process tended to fill up the rough structures of the SiO_2 matrix, retaining the external surface area of the SiO_2 particles. The t-plot of **5c** 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**, **5a**, **5b**, and **5c**. 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 SiO_2 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 SiO_2-matrix overlayers, the Mn 2p peaks were observed to get smaller. Even the Mn 2p peaks of **5a** entirely disappeared, as did those of **5b** and **5c** (Figure 4(B)). Considering the escape depth of Mn 2p, these results clearly indicated that the supported Mn clusters on the surface of the SiO_2 particles were closely surrounded by the produced SiO_2-matrix overlayers.

It was found out that the structure of **5c** after stacking of the SiO_2-matrix overlayers was different from that of **2**. Mn K-edge EXAFS found the local coordination structure of the supported Mn species on **5c**: Mn···Mn interaction length of 0.301 ± 0.008 nm (CN = 0.7 ± 0.3) and two Mn−O interactions at 0.185 ± 0.006 nm (CN = 1.4 ± 1.7) and 0.221 ± 0.013 nm (CN = 1.0 ± 1.8) (Table 1, Figure 3 and Supporting Information, Figure S4). The amount of remaining CH_3COO ligands of **5c** was estimated to be 2.0 equiv to Mn_4. In the DR-UV/vis spectrum of **5c**, the characteristic peaks attributed to d-π^* 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 SiO_2-matrix overlayers. Therefore, a possible composition of dimeric Mn species on **5c**

Table 2. Catalytic Performances of Mn Catalysts for Epoxidation of Alkenes[a]

Entry	Catalyst	Reactant	Mn$_4$/Reactant/IBA	Time /h	Conversion %[b]	Selectivity %[c]	Leaching of Mn /%[d]
1	--		0/500/1500	72	0	--	--
2	SiO$_2$[e]		0/500/1500	72	0	--	--
3	**1**		1/500/1500	4	97	94	--
4	**2**		1/500/1500	6	97	96	45.8
5	**3**		1/500/1500	6	99	96	53.4
6	**4**	[structure] f	1/500/1500	11	99	97	47.3
7	**5a**		1/500/1500	33	89	91	0.41
8	**5b**		1/500/1500	24	94	88	0.02
9	**5c**		1/500/1500	31	97	91	0.01
10	**5c**		1/500/0	72	0	0	--
11	**5c**[g]		1/500/1500	72	0	0	--
12	**6**		1/500/1500	12	99	97	38.6
13	**7**		1/500/1500	36	~0	n.d.	--
14	**5c**	[structure] h	1/500/1500	15	92	82	--
15	**5c**	[structure] h	1/500/1500	9	85	91	--
16	**5c**	[structure]	1/500/1500	5.5	97	93	--
17	**5c**	[structure] i	1/500/1500	9.5	46	55	--

[a]Reaction conditions: Mn$_4$, 0.67×10^{-6} mol; Mn$_4$/reactant/biphenyl/IBA = 1/500/250/1500; CH$_2$Cl$_2$, 3 mL; 283 K; O$_2$, 101.3 kPa. Biphenyl was used as an internal standard. [b]Conversion % = (Initial mole of reactant − Residual mole of reactant)/Initial mole of reactant × 100%. [c]Selectivity % = Mole of epoxide product/(Initial mole of reactant − Residual mole of reactant) × 100%. [d]The leaching of Mn was detected by ICP spectroscopy of the reaction mixture filtrate after the reaction. [e]The amount of SiO$_2$ was 25 mg. [f]Benzaldehyde was formed as a byproduct. [g]The reaction was conducted under N$_2$ atmosphere. [h]α,β-Unsatrated ketone was formed as a byproduct. [i]1-Heptanal and 3-octenone were formed as a byproduct. n.d.: not determined.

could be written as $[Mn_2(CH_3COO)]_{2x}$, 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 O$_2$ and IBA (a sacrificial reagent)[33] 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 SiO$_2$-supported Mn clusters, **2−4**, showed activity and high selectivity over 95% (entries 4−6), whereas SiO$_2$ 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 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 SiO$_2$-matrix overlayers on the SiO$_2$-supported Mn clusters imparted the catalyst with remarkable stability (Table 2). The supported Mn catalysts with the SiO$_2$-matrix overlayers (**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 SiO$_2$-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.[36]

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 SiO$_2$ particle surface on the catalysts **3** and **5c** after they were recycled 5 times. On **3** without the SiO$_2$-matrix overlayers, the conversion decreased significantly because of the extensive leaching of Mn species into solution. After 2 cycles of
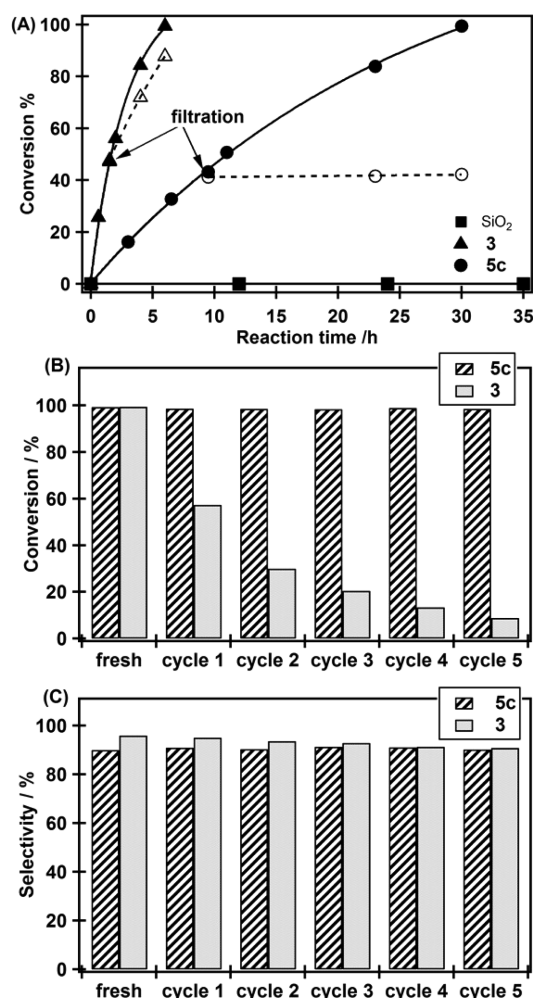
Figure 5. (A) Test of the heterogeneous nature of the catalysts in *trans*-stilbene epoxidation. ((B), (C)) Recycling tests of **3** (for 6 h) and **5c** (for 30 h) in *trans*-stilbene epoxidation. (B) Conversion of each cycle; (C) selectivity for epoxide; reaction conditions: Mn$_4$, 0.67×10^{-6} mol; Mn$_4$/*trans*-stilbene/IBA = 1/500/1500; CH$_2$Cl$_2$, 3 mL; 283 K; O$_2$, 101.3 kPa.

epoxidation, 80% of the supported Mn clusters were lost (Supporting Information, Figure S8). On the other hand, the leaching of the Mn catalyst on **5c** with the SiO$_2$-matrix overlayers was negligible after 6 epoxidation cycles, and the conversion of *trans*-stilbene remained >90%, keeping up with the high epoxide selectivity. The differences were obvious between **3** and **5c**, demonstrating the positive effect of the surface SiO$_2$-matrix overlayers on the stability of the supported Mn epoxidation catalysts.

Other alkenes were smoothly converted to epoxides on **5c** (Table 2). Observed major byproducts were aldehydes from C=C bond cleavage and ketones from oxidation at the α-position. The reactions of internal alkenes such as cyclohexene, cyclooctene, and norbornene produced epoxides with high selectivity, whereas the selectivity of terminal alkene such as 1-octene was low, forming 1-heptanal and 3-octenone as byproducts.

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.[33a] The epoxidation of cholesteryl benzoate provides two epoxide

products, α-epoxide and β-epoxide (Scheme 1). In the case of autoxidation using peroxo species (e.g., *m*-CPBA), α-epoxide is

Scheme 1. Epoxidation of Cholesteryl Benzoate
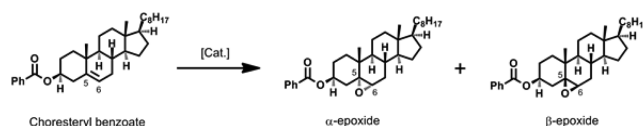
preferably produced. Analogously, if a free peroxo species were to be formed on the Mn site, but reacted independently with an alkene reactant in solution (in a similar way as autoxidation), the selective formation of α-epoxide would also be observed. On the other hand, if the epoxidation step were to proceed on a metal site, 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 O$_2$/IBA system.[33a] For instance, the α-epoxide/β-epoxide product ratio on bis-(acetylacetonato)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 ^{1}H NMR), which agreed with reported results.[33a] 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 SiO$_2$-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^{-2} 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 SiO$_2$-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 SiO$_2$-matrix overlayers. Since the structure of Mn species on **5c** was totally different from that on **3**, the loss of CH$_3$COO and bipy ligands, the addition of surface silanol groups, and the existence of SiO$_2$-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 MnO$_x$ as supported species. Catalyst **7** was prepared by subsequent stacking of SiO$_2$-matrix overlayers on **6** with MnO$_x$ 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 SiO$_2$-matrix overlayers on the MnO$_x$ 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 Mn$_4$ clusters (**1** and **2**) during the preparation step of the SiO$_2$-matrix overlayers, the catalyst **5c** prepared on **2** with the Mn cluster with the several coordinating ligands cannot be obtained from the simple supported MnO$_x$ species on the SiO$_2$ 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 SiO$_2$-matrix overlayers would cooperatively achieve robust catalysis in the heterogeneous phase.

4. CONCLUSIONS

The functionalization of the surface of SiO$_2$ particles with attached $[Mn_4O_2(CH_3COO)_7(bipy)_2](ClO_4)\cdot 3H_2O$ (**1**) and the stacking of SiO$_2$-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 SiO$_2$ 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 SiO$_2$-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 SiO$_2$-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 SiO$_2$-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, ^{29}Si NMR spectra, N$_2$ 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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