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XAFS Characterization of Surface-functionalized Mn Catalysts for Alkene Epoxidation

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Introduction

A Mn_4 oxonuclear complex was chemically attached on a SiO_2 surface and its surface was chemically functionalized by SiO_2-matrix overlayers toward the significant improvement of durability for the supported Mn-cluster catalysts under selective epoxidation conditions. The local coordination structures of supported Mn cluster complex catalysts and SiO_2-matrix functionalized Mn cluster complex catalysts that remarkably improved the durability of the Mn-cluster catalyst from leaching, were investigated by Mn K-edge XAFS.

Experimental

A SiO_2-supported Mn cluster (**2**) was prepared by the attachment of a Mn oxotetranuclear cluster complex $[Mn_4O_2(CH_3COO)_7(bipy)_2](ClO_4)\cdot 3H_2O$ (**1**) on a SiO_2 surface. A SiO_2-matrix functionalized Mn cluster (**3**) was prepared by the hydrolysis-polymerization of tetramethoxysilane and H_2O at 358 K and successive evacuation at 373 K on **2**. Mn K-edge XAFS was measured at 20 K at the BL9C and BL12C stations with a Si(111) double-crystal monochromator. **1** and SiO_2-supported Mn catalysts were measured in transmission mode, and Mn catalysts protected by SiO_2-matrix overlayers were measure in fluorescence mode. EXAFS spectra were analysed using ATHENA and ARTEMIS programs. k^3-Weighted EXAFS oscillations were Fourier transformed into *R*-space, and 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). Phase shifts and backscattering amplitudes for Mn···Mn and Mn-O/N were calculated by the FEFF8 code.

Results and Discussion

The local coordination structures of the SiO_2-supported Mn cluster complexes were examined by Mn K-edge EXAFS analysis, whose structural parameters are listed in Table 1. Mn K-edge EXAFS of **2** showed that the CN of the long Mn···Mn interaction (0.335 ± 0.007 nm) was decreased to a half (from 2.0 to 1.0), while the CN of short Mn···Mn interaction remained almost the same (from 0.5 to 0.8) compared with Mn K-edge EXAFS of **1**, suggesting the distortion of the original Mn_4 cluster framework on the SiO_2 surface.

Mn cluster structure was maintained even after SiO_2-matrix overlayers were stacked around the SiO_2 surface of **2**. Mn K-edge EXAFS of **3** exhibited Mn···Mn interaction at 0.301 ± 0.008 nm (CN = 0.7 ± 0.3) and two Mn–O(N) interactions at 0.185 ± 0.006 nm and 0.222 ± 0.013 nm. The amount of remained CH_3COOH ligands of **3** was estimated to be 2.0 equiv. to Mn_4. These results indicated that the partial release of the coordinating ligands brought about the further distortion of the supported Mn cluster in the SiO_2-matrix overlayers.

2 was active for the epoxidation of *trans*-stilbene (conversion: 97%, epoxide selectivity: 96% for 6 h), however, the attached Mn cluster was easily released to a reaction solution under the epoxidation conditions (Mn leaching: approximately 50%). After the functionalization by stacking of surface SiO_2-matrix overlayers surrounding the supported Mn cluster remarkably improved catalyst durability. The Mn leaching of **3** was reduced to the minimum value of 0.01% while maintaining stable epoxidation performances in the heterogeneous phase (conversion: 97%, epoxide selectivity: 91% for 31 h).

Table 1 Structural parameters of the supported Mn complexes obtained by curve-fitting analyses of Mn K-edge EXAFS measured at 20 K[a]

Shell	CN	*R* /nm	ΔE_0	σ^2 /$\times 10^5$ nm^2
2. SiO_2-supported Mn cluster (Mn: 2.2 wt%) [b]				
Mn···Mn	0.8 ± 1.0	0.286 ± 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-matrix functionalized Mn cluster (Mn: 0.7 wt%) [c]				
Mn···Mn	0.7± 0.3	0.301 ± 0.008	14 ± 11	9
Mn–O/N	1.4 ± 1.7	0.185 ± 0.006	3 ± 9	2 ± 8
Mn–O/N	1.0 ± 1.8	0.222 ± 0.013	14 ± 21	2 ± 8

[a] S_0 was fitted to be 0.82 from the curve-fitting analysis of **1**. [b] k = 30 – 120 nm^{-1}, R = 0.08 – 0.34 nm, R_f = 0.5%. [c] k = 30 – 110 nm^{-1}, R = 0.07 – 0.30 nm, R_f = 1.6%.

Reference

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