Supplementary Information

Creation of a high-valent manganese species on hydrotalcite and its application to the catalytic aerobic oxidation of alcohols

Kohji Nagashima,^{*a*} Takato Mitsudome,^{*a*} Tomoo Mizugaki,^{*a*} Koichiro Jitsukawa,^{*a*} and Kiyotomi Kaneda^{**a*, *b*}

^a Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka, 560-8531, Japan.
E-mail: kaneda@cheng.es.osaka-u.ac.jp; Fax: +81 6-6850-6260; Tel: +81 6-6850-6260
^b Research Center for Solar Energy Chemistry, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka, 560-8531, Japan

Contents

Experimental	28
EXAFS spectra of Mn/HT- <i>Ox</i>	4S
A plausible reaction path	58
References	68

Experimental

1) General

All organic reagents were purified before use.¹ MnCl₂·4H₂O was purchased from Wako Pure Chemical Co., Ltd. as special grade, and used as received. MnO, Mn₂O₃, and MnO₂ were purchased from Merck Chemical Industries Co., Ltd. as reference compounds. Gas chromatography (GC-FID) was carried out on a Shimadzu GC-2014 equipped with a KOCL-3000T column (2 m). X-ray diffraction (XRD) was measured with an X'pert diffraction meter (Phillips Co., Ltd.).

2) Stoichiometric reaction of 1 using Mn/HT-Ox

Mn/HT-Ox (0.6 g, Mn: 0.18 mmol) was placed in a reaction vessel equipped with a reflux condenser, followed by addition of degassed toluene (8 mL) and **1** (0.21 mmol). The reaction mixture was vigorously stirred at 100 °C under an inert atmosphere of Ar for 12 h in a glove box.

3) A typical procedure for the oxidation of 1 by Mn/HT-Ox

Mn/HT-Ox (0.2 g, Mn: 0.06 mmol) was placed in a reaction vessel equipped with a reflux condenser, followed by addition of toluene (8 mL) and **1** (1 mmol). After the reaction mixture was vigorously stirred at 100 °C under atmospheric pressure of O₂ for 12 h, Mn/HT-Ox was removed by centrifugation and the yield was determined by GC analysis with biphenyl as an internal standard.

4) X-ray Absorption Fine Structure (XAFS) Measurements

The Mn K-edge X-ray absorption data were collected in the quick mode and recorded at room temperature in transmission mode at the facilities installed on the BL-01B1 line of

SPring-8, Japan Atomic Energy Research Institute (JASRI), Harima, Japan, using a Si(111) monochromator (proposal number: 2009B1506). The ordinate scale of the XANES spectra was normalized at 500 eV above the adsorption edge, where the differences in the XAFS oscillations among the spectra were negligible.² The Mn K-edge position was taken as the first major peak in the corresponding derivative XANES spectrum. The XAFS data were normalized by fitting the background absorption coefficient around the energy region higher than the edge about 35-50 eV with the smoothed absorption of an isolated atom. Fourier transformation (FT) of k^3 -weighted normalized XAFS data was performed over the 3.0 < k/Å < 12 range to obtain the radial structure function. CN (the coordination number of scatterers), *R* (the distance between an absorbing atom and scatterer), and Debye-Waller factor were estimated by curve-fitting analysis with an inverse FT assuming a single scattering. The Structural parameters were determined by curve-fitting procedures with RIGAKU REX2000 ver. 2.5.7 data analysis software.

EXAFS spectra of Mn/HT-Ox



Fig. 1S Fourier transformation (FT) of the k^3 -weighted K-edge EXAFS spectrum of (a) Mn/HT, (b) Mn/HT-Ox, (c) reduced Mn/HT-Ox with alcohol under Ar, (d) re-oxidized Mn/HT-Ox under air, and (e) reduced Mn/HT-Ox with alcohol under Ar after re-oxidation.

shell	CN ^[a]	R/Å ^[b]	$\Delta\sigma$ / Å ^{2 [c]}
Mn-O	6.065	1.905	0.0081
Mn-Mn	3.611	2.913	0.0021

Table 1S Results of Curve-Fitting Analysis of Mn/HT-Ox

^[a] Coordination number. ^[b] Interatomic distance. ^[c] $\Delta \sigma$ is the difference between the Debye-Waller factor of Mn/HT-Ox and that of the reference sample.

A plausible reaction path

On the basis of the stoichiometric oxidation of alcohols using Mn compounds proposed

by Goldman, we proposed a plausible reaction path as follows.³



References

- D. D. Perrin, W. L. F. Armarego (Eds.), *Purification of Laboratory Chemicals*, third ed., Pergamon Press, Oxford, UK, 1988.
- 2. Y. Terada, K. Yasaka, F. Nishikawa, T. Konishi, M. Yoshio, I. Nakai, J. Solid. State Chem., 2001, 156, 286.
- 3. I. M. Goldman, J. Org. Chem., 1969, 34, 3289.