XAFS Analysis for Calcination Process of Supported Mn Catalysts on Silica

Kazutaka Furusato, Misaki Katayama, and Yasuhiro Inada
Department of Applied Chemistry, Graduate School of Life Sciences, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu, Shiga 525-8577, Japan

Abstract

The calcination process of the silica-supported Mn catalysts was investigated by means of *in-situ* XAFS technique using various Mn precursors. The hydrated Mn salts were first formed on silica after drying at 60 °C for all Mn precursors, and were oxidized to various Mn oxides except for $MnSO_4$ as the precursor. The Mn species was changed from hydrate to Mn_2O_3 via Mn_3O_4 during the calcination process in the cases of $MnCl_2$ and $Mn(CH_3CO_2)_2$, whereas MnO_2 formed initially was reduced to Mn_3O_4 via Mn_2O_3 even in air when the nitrate anion coexisted.

1. Introduction

The product generation and the maintenance of the environment in modern chemical industry are supported by the effective chemical conversion using the heterogeneous metal catalysts. The noble metal catalysts, such as Pt, Rh and Pd, are widely utilized because they have high catalytic activity for various reactions. However, it is an urgent problem for modern society to find alternative metal catalysts due to their high cost and rarity.

It has been reported that the Al_2O_3–supported Mn catalysts show high activity for the decomposition of volatile organic compounds [1]. The catalytic efficiency for CO oxidation and oxidative coupling of methane has been investigated using Mn_xO_y/SiO_2 catalysts [2,3]. It is widely known that the Mn oxide takes various oxidation states, such as MnO (+2), Mn_3O_4 (+2.6), Mn_2O_3 (+3), and MnO_2 (+4). In addition, the oxyanions with higher oxidation states also exist, such as MnO_4^{3-} (+5), MnO_4^{2-} (+6), and MnO_4^{-} (+7). The catalytic performance is largely affected by the oxidation state of the supported Mn species, and its control can change the activity of the Mn catalysts and the selectivity of the products. Thus, the speciation of supported species is fundamental to understand the catalysis performance of the Mn catalysts.

A most typical preparation method is the impregnation of the Mn salts on supporting materials. The calcination in air is then adapted to the supported precursor to complete the catalyst preparation. During the calcination process, the chemical conversion is expected to the Mn species. In this study, the calcination process of the SiO_2-supported Mn species was investigated using the X-ray absorption fine structure (XAFS) spectroscopy, which is very useful to know the local structure and the electronic state under reaction conditions. The effect of the counter anion in the used Mn salts was systematically evaluated.

2. Experimental

The samples were prepared by the impregnation method using silica (JRC-SIO-10) distributed from the Catalysis Society of Japan. The Mn salt, $Mn(NO_3)_2 \cdot 6H_2O$ (**MnN**), $MnCl_2 \cdot 4H_2O$ (**MnC**), $Mn(CH_3CO_2)_2 \cdot 4H_2O$ (**MnA**), and $MnSO_4 \cdot 5H_2O$ (**MnS**), was dissolved in acidic aqueous solution, and the SiO_2 powder was suspended in the solution so as the Mn loading to be 10 wt%. The mixture was for 1 h at 30 °C and was dried for 60 h at 60 °C. The catalyst preparation is normally completed by the calcination at 600 °C in air.

The *in-situ* XAFS measurements were carried out at BL-3 of the SR center (Ritsumeikan University) and BL-12C of Photon Factory (KEK) at the Mn K edge in the transmission mode.

The Si(220) and Si(111) double-crystal monochromator was used at BL-3 and BL-12C, respectively. The higher-order harmonics at the latter was removed by a Ni-coated double-mirror system.

The powder of the catalyst precursor dried at 60 °C was set in a flow-type *in-situ* cell, and the temperature was changed from 25 to 600 °C with the increase rate of 10 °C/min under the dilute O_2 gas flow (10 vol% balanced by He) with the flow rate of 100 cm^3/min. The quick-scanning XAFS measurements were repeated in the X-ray energy range from 6.03 to 7.10 keV with the interval time of 2 min.

3. Results and discussion

3.1. Supported Mn species before calcination

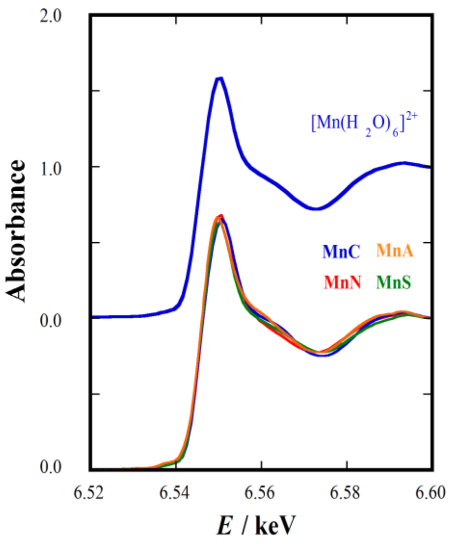

Figure 1. XANES spectra of the Mn precursor powders compared with that of aqueous solution.

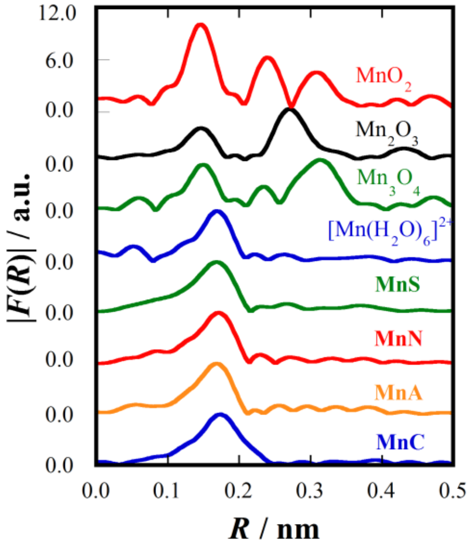

Figure 2. Fourier transform functions of the Mn precursor powders.

Figure 1 shows the XANES spectra of the Mn precursor powders dried at 60 °C. The edge energy is in accordance with those of divalent Mn species, and all XANES spectra are in agreement with that of aqueous solution of Mn^{2+}, in which the Mn(II) ion is hydrated by 6 water molecules to form $[Mn(H_2O)_6]^{2+}$. The supported hydrated Mn species is independent of the counter anion of used Mn salt. The EXAFS analysis revealed that the Mn–O bond length was 0.218 ± 0.005 nm for all precursors (see Figure 2), and no interactions were observed in the longer distance range, indicating the isolated precipitation of $[Mn(H_2O)_6]^{2+}$ on SiO_2 without any direct brides between Mn(II) centers.

3.2. Oxidation of the supported Mn species during calcination

The XANES spectral change during the calcination process is presented in Figure 3 for the supported precursor of **MnN**. The absorption edge of the initial spectrum of Mn(II) hydrate was blue shifted as the temperature increased, and the final spectrum was almost in agreement with that of MnO_2. Because the XANES spectrum at intermediate temperature was similar to that of Mn_2O_3, the complex variation of oxidation states was expected during the calcination process.

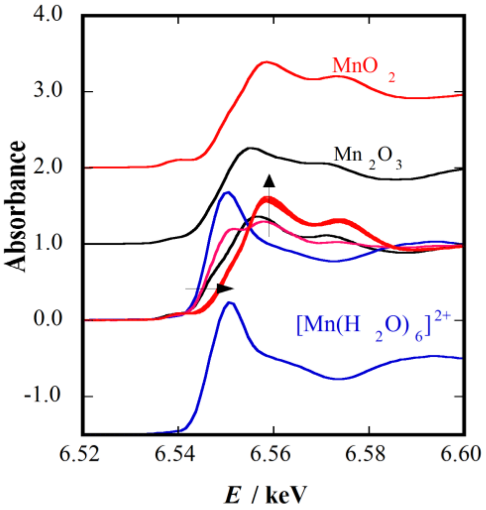

Figure 3. XANES spectral change for calcination process of supported precursor of **MnN**.

The composition of the supported Mn species was analyzed by the linear combination fitting of the XANES spectrum by using those of standard samples with various oxidation states. Figure 4 shows the temperature dependence of the mole fraction for all samples with the different anion in the supported precursor, and demonstrates that the oxidation route of the Mn species is different by the coexisting anion.

In the case of **MnC** as shown in Figure 4(A), the supported Mn(II) hydrate was first oxidized to Mn_3O_4 at about 300 °C, and it was further oxidized to Mn_2O_3, which was major species at 600 °C. The oxidation proceeded in order from +2 to +2.6 to +3. A similar ordered oxidation was observed for **MnA** as shown in Figure 4(B) with a different final composition at 600 °C, where Mn_3O_4 was still a major species.

In the case of **MnN** as shown in Figure 4(C), the supported Mn(II) hydrate was directly oxidized to MnO_2 with the oxidation number of +4 at a moderate temperature range from 200 to 500 °C. The MnO_2 species was not stable at higher temperature range than 600 °C, and was reduced to Mn_2O_3 and then Mn_3O_4 even under the flow of oxygen. The reduction of MnO_2 at high temperature is also known for bulk MnO_2 powder, and it is changed to Mn_2O_3 at 500–600 °C by the thermal dissociation of oxygen.

Figure 4(D) shows the composition for **MnS** versus temperature. It was interestingly clarified that there was no change in the composition and that the valence state of the Mn species was kept to be +2. The absorption edge was not shifted during the calcination process,

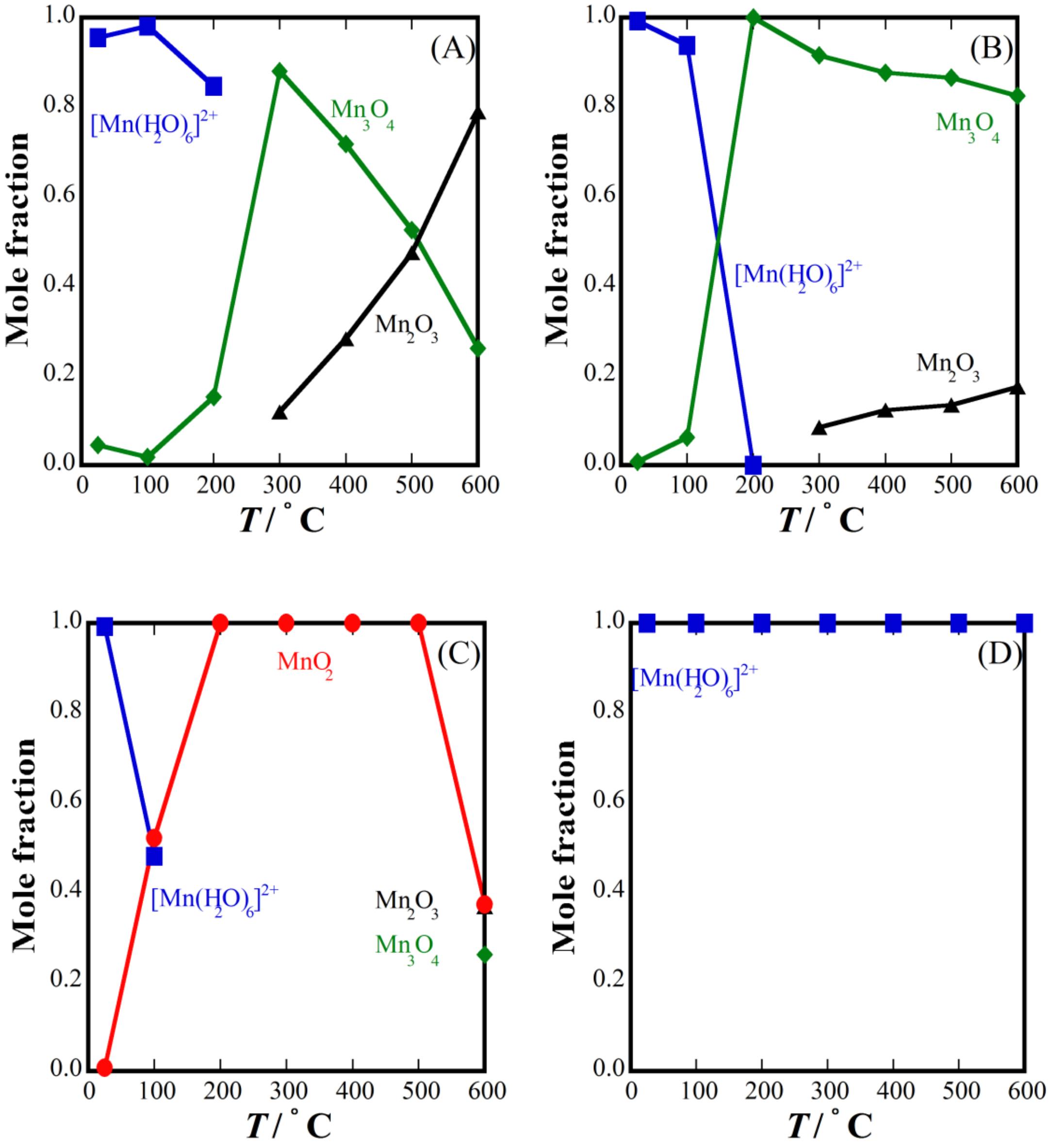

Figure 4. Temperature dependence of mole fractions of the supported Mn species for **MnC** (A), **MnA** (B), **MnN** (C), and **MnS** (D). The blue squares, green diamonds, black triangles, and red circles denote the Mn(II) hydrate, Mn_3O_4, Mn_2O_3, and MnO_2, respectively.

whereas the XANES spectrum was slightly changed as the temperature increased. Because it is well known that the hydrated water in sulfate salts dissociates at 400 °C, the supported Mn(II) hydrate is considered to change to anhydrous sulfate on SiO_2 during the calcination process.

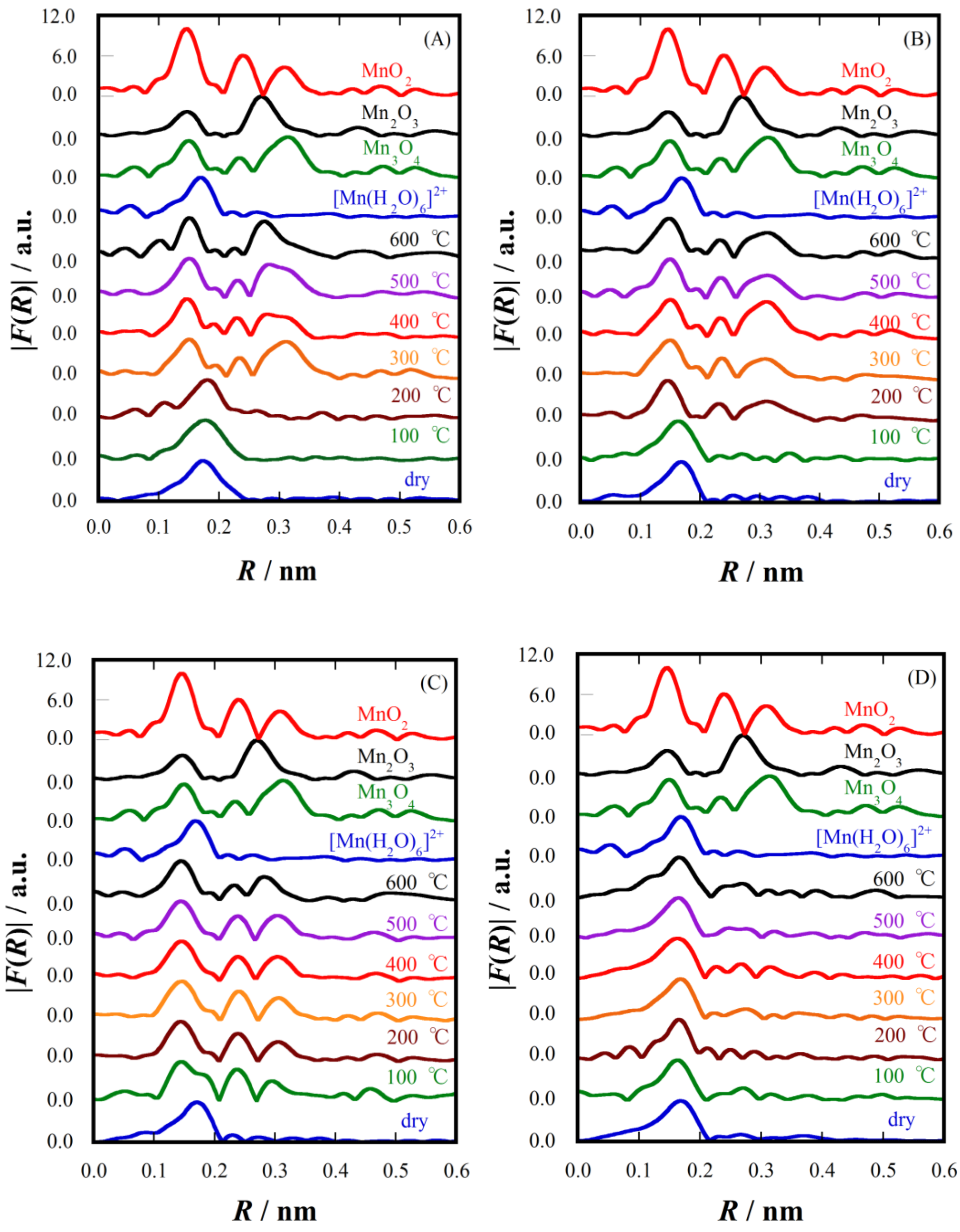

Figure 5. Fourier transform functions of the EXAFS oscillations of the supported Mn species for **MnC** (A), **MnA** (B), **MnN** (C), and **MnS** (D) as a function of temperature.

Figure 5 shows the change in Fourier transform functions of the EXAFS oscillations as a function of temperature. All changes observed in Figure 5 are in accordance with the composition changes versus temperature described above. Figure 5 indicates that the Mn species are estimated according to the shape of Fourier transform functions at the distance range of 0.25–0.40 nm.

4. Conclusion

The calcination process was investigated for the supported Mn catalysts by varying the counter anion of the Mn salt. The formed Mn oxides during the calcination are drastically different in response to the coexisting anion. Any Mn oxides are not formed when the Mn sulfate is used, and the anhydrous sulfate is formed instead. In the cases of chloride and acetate, the hydrate Mn(II) species is oxidized to Mn_3O_4 and Mn_2O_3, whereas MnO_2 is first generated for nitrate and is reduced to Mn_2O_3 and then Mn_3O_4 even under the oxidative atmosphere. This reduction suggests the instability of MnO_2 at higher than 600 °C. Therefore, the supported MnO_2 catalyst is prepared by using only the Mn nitrate. The present results are very important for the valence-controlled preparation of the supported Mn catalysts.

Acknowledgment

The XAFS measurements at PF were carried out under the approval of the Photon Factory Program Advisory Committee (Proposal No. 2013G596) of High Energy Accelerator Research Organization.

Reference

[1] G. S. Pozan, *J. Haz. Mat.*, **221-222**, 124 (2012).

[2] Y. F. Han, F. Chen, Z. Y. Zhomg, K. Ramesh, E. Widjaja, and L.W. Chen, *Catal. Commun.*, **7**, 739 (2006).

[3] A. Chen, H. Xu, W. Hua, W. Shen, Y. Yue, and Z. Gao, *Topics Catal.*, **35**, 1 (2005).