Mem. SR Center Ritsumeikan Univ. No. 27, 9-13 (2025)

In situ XAFS Analysis for Manganese Oxide Catalysts Supported on Silica in its Preparation and Thermal Decomposition Processes

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The change in the chemical state of the Mn species supported on SiO_2 was analyzed by the XAFS method. It was found that in the early stage of the drying process to prepare the catalyst, the Mn(II) hexahydrate was supported on SiO_2 and was oxidized to MnO_2 by drying in air for more than 5 days even at 60 °C. *In situ* XAFS analysis of the oxygen emission process of MnO_2 to form Mn_2O_3 was carried out under various O_2 content in the atmosphere. It was clarified that the conversion temperature from MnO_2 to Mn_2O_3 was sensitive to the O_2 content. The conversion temperature shifted sharply to higher temperatures when the O_2 content was in the range of 0 to 2 vol%, indicating that this temperature responds sensitively to the O_2 content. At O_2 contents above 2 vol%, the change in conversion temperature was suppressed, and the conversion temperature with respect to the O_2 content tended to converge to a constant value.

1. Introduction

The Mn-based oxides are the promising catalysts for the catalytic oxidation of volatile organic compounds (VOCs). Because VOCs cause pollution such as ozone consumption in the stratosphere and carcinogenicity, it is very important to adopt appropriate removal technologies of VOCs [1], and the activities of various Mn-based oxide catalysts for catalytic oxidation of VOCs have been intensively studied [2-5]. It is known that the valence state of Mn has an important effect on the decomposition activity of VOCs, in addition to the structure, the crystal phase, the morphology, and the crystal facets of the Mn-based oxide catalysts. The most typical manganese oxide is MnO_2, whereas it has been reported that the decomposition activity of VOCs follows the order $Mn_3O_4 > Mn_2O_3 > MnO_2$ [5]. Therefore, elucidating the changes in the chemical state of the Mn species during the preparation of Mn-based oxide catalyst and the heat treatment is important for constructing highly active catalytic systems.

In this study, SiO_2-supported manganese oxide catalysts were prepared by the incipient wetness method using Mn(II) nitrate as a precursor and were characterized by X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS) measurements. *In situ* XAFS measurements were then performed for the deoxygenation process of the manganese oxide catalysts under the elevated temperatures. The changes in the chemical state that occur during the calcination stage in the preparation of the manganese oxide catalysts were clarified. We found the relationship between the manganese species and the treatment conditions (O_2 content in the gas environment and calcination temperature). The calcination conditions to select the supported manganese species (MnO_2 and Mn_2O_3) were proposed.

2. Experimental

Sample preparation

$Mn(NO_3)_2\cdot 6H_2O$ was purchased from Fujifilm Wako Pure Chemical. The SiO_2 used was that (JRC-SIO-10) distributed by Catalysis Society of Japan as a reference catalyst with the specific surface area and the pore volume of 200 m^2/g and 1.0 cm^3/g, respectively. An aqueous solution of $Mn(NO_3)_2\cdot 6H_2O$ was added to SiO_2, and the volume of the solution was set to the condition of incipient wetness for the SiO_2 powder used. The concentration of the aqueous solution was adjusted so that the amount of supported MnO_2 was 20 wt%. The sample was dried at 60 °C. The portion of the sample was taken each day to offer the XRD and XAFS analyses. The total drying time was 8 d.

Characterization

The XRD measurements were performed using the Ultima IV diffractometer (Rigaku) using Cu K_α radiation. The diffraction intensities were recorded in the 2θ values between 10° and 80°. The loading amount of MnO_2 was determined by the X-ray fluorescence analysis (XRF) using the Supermini fluorescent X-ray spectrometer (Rigaku). A calibration curve was obtained using prepared samples in which a known amount of MnO_2 was physically mixed with SiO_2.

In situ XAFS measurements

The *in situ* XAFS measurements at the Mn K edge were carried out for the heating processes in the transmission mode at BL-3 of the SR Center (Ritsumeikan Univ.). They were performed under the O_2 gas flow diluted by He with the total flow rate of 100 cm^3/min. The O_2 content in the gas environment was varied from 0 vol% to 10 vol%. The heating rate was 10 °C/min, and the temperature was maintained by stopping the heating during the XAFS measurement. The amount of sample required for the

XAFS measurements at the Mn K edge was estimated based on the absorption coefficient and filled into a quartz glass ring with the inner diameter of 7 mm. Then, the ring was placed in a flow-type *in situ* XAFS cell.

The background absorptions in the pre- and post-edge region of the X-ray absorption near edge structure (XANES) spectrum were calculated using the Athena code [6]. The background absorptions were subtracted from the observed data and the normalized XANES spectrum was obtained by dividing the subtracted data by the absorption edge jump. The linear combination fitting (LCF) analysis was performed using the normalized XANES spectrum to determine the sample composition.

3. Results and Discussion

3.1. Chemical state of dried sample

Figure 1(A) shows the results of XRD measurements of samples dried at 60 °C for different days. It was confirmed that the diffraction lines of MnO_2 appeared in the samples after drying for 3 days or more. The XRD patterns of the samples dried for 5 to 8 days were almost identical to that of β-MnO_2, except that the diffraction line intensity of the (110) plane was significantly low. For sample with drying times shorter than 3 days, no diffraction lines originating from the Mn species were observed, suggesting that the Mn species existed in an amorphous state.

The XANES spectra at the Mn K edge of these samples are shown in Fig. 1(B). The absorption peak at 6.550 keV was characteristic of the aqueous solution of Mn(II) nitrate and was observed in samples dried for 4 days or less. Its intensity tended to decrease with increasing drying time. It was found that in the early stage of the drying process, the Mn(II) hexahydrate was directly supported on SiO_2 with nitrate ions as the counter ions. The XANES spectrum changed drastically between 4 and 5 days of drying, eventually matching the spectrum of MnO_2 with a white line at 6.558 keV. It was found that Mn(II) nitrate hexahydrate supported on SiO_2 could be oxidized to MnO_2 by drying in air for more than 5 days even at 60 °C. The change in the chemical state of the Mn species was not completely linear with respect to drying time, which is expected to be due to temperature imbalance in the sample powder during the drying process.

The MnO_2 loading of the samples dried at 60 °C for 6 d was determined by the XRF analysis. The calibration curve is shown in Fig. 1(C) obtained by plotting the X-ray fluorescence intensity versus the MnO_2 content of the standard samples. The X-ray fluorescence intensity observed for the dried sample derived the loading of MnO_2 to be 21.1 wt%.

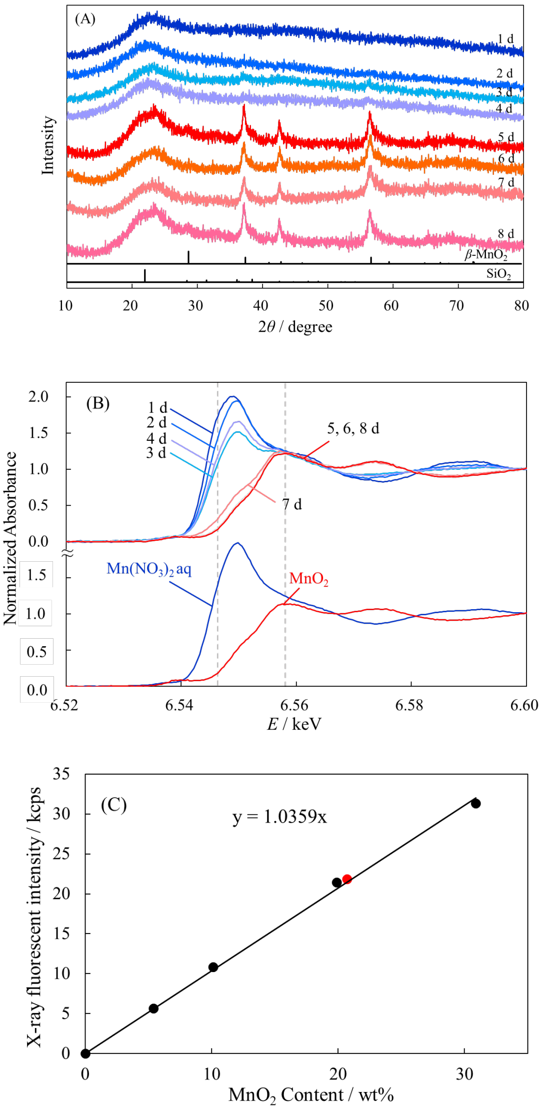

Fig. 1. The characterization of the prepared sample by the XRD pattern (A) and the XANES spectra (B). The loading of MnO_2 was determined by the XRF measurement based on the calibration curve depicted in (C).

3.2. Oxygen emission process of MnO_2 at elevated temperature

Figure 2(A) shows the XANES spectral change during the heating process under pure He atmosphere. The spectrum from room temperature to 300 ºC is consistent with that of MnO_2. Above 350 ºC, the absorption edge shifted to the lower energy side, and the spectrum above 490 ºC was consistent with that of Mn_2O_3. As the temperature increased to 678 ºC, the white line peak intensity was slightly increased, whereas the energy of the absorption edge was almost constant.

The mole fraction of the Mn species was determined by a liner combination fitting (LCF) analysis of the observed XANES spectrum. In this

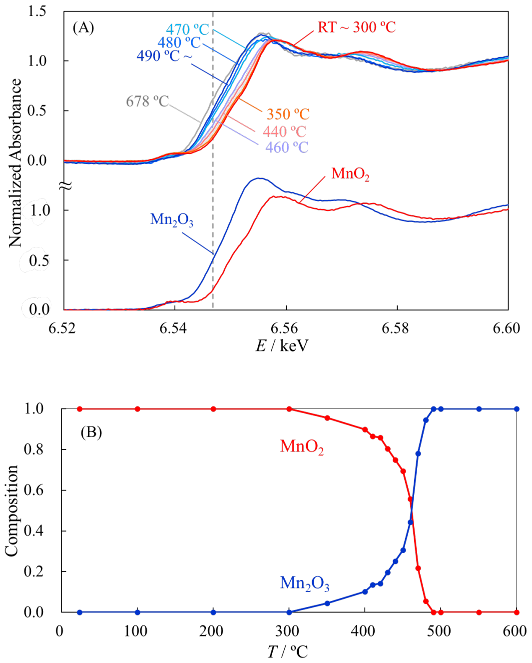

Fig. 2. The change of XANES spectrum (A) and the mole fraction of the Mn species (B) during the heating process at 0 vol% O_2.

study, the spectrum measured at room temperature for MnO_2, and the spectrum measured at 490 °C for Mn_2O_3 were used as the standards for the LCF analysis. The determined values of mole fraction were plotted in Fig. 2(B) as a function of temperature. MnO_2 existed quantitatively up to 300 °C, and the reduction reaction to Mn_2O_3, eq. (1), proceeded gradually in the temperature range from 300 °C to 420 °C.

$$4MnO_2 \rightarrow 2Mn_2O_3 + O_2 \tag{1}$$

A sharp change in the composition was observed from 420 °C to 490 °C, and the Mn_2O_3 state was maintained at higher temperatures. It was found that MnO_2 supported on SiO_2 spontaneously proceeded a reduction reaction (oxygen emission process) to Mn_2O_3 when heated. When the conversion temperature is defined as the temperature at which MnO_2 and Mn_2O_3 exist in equal amounts, the conversion temperature at 0 vol% O_2 in the atmosphere was determined to be 455 °C.

The results of a similar *in situ* XAFS analysis were given in Fig. 3 when the O_2 content in the atmosphere was set to 1 vol%. The temperature range in which the MnO_2 state is maintained was clearly extended to higher temperatures, and the oxygen emission process of MnO_2 to form Mn_2O_3 proceeded in the temperature range around 520 °C. Because it was completely converted to Mn_2O_3 at 540 °C, the conversion temperature was regarded to be 520 °C, and it was shown that an increase in O_2 content of only 1 vol% suppressed the oxygen emission process

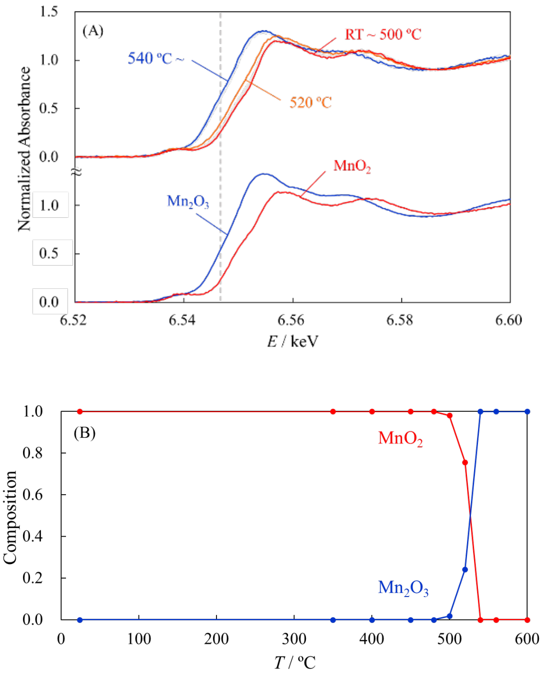

Fig. 3. The change of XANES spectrum (A) and the mole fraction of the Mn species (B) during the heating process at 1 vol% O_2.

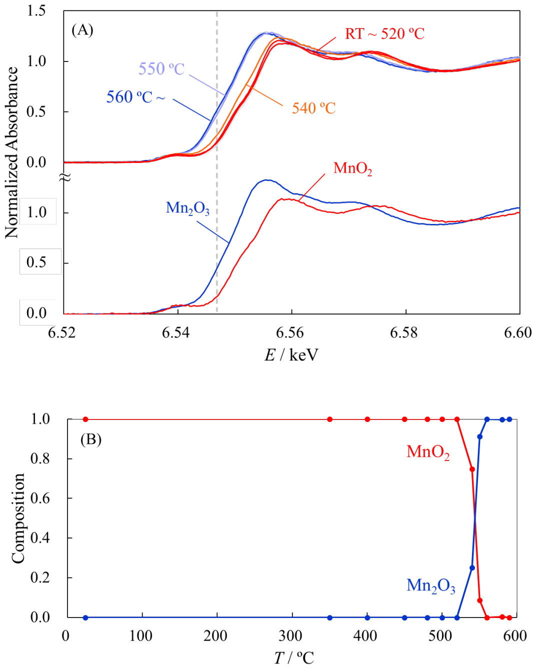

Fig. 4. The change of XANES spectrum (A) and the mole fraction of the Mn species (B) during the heating process at 5 vol% O_2.

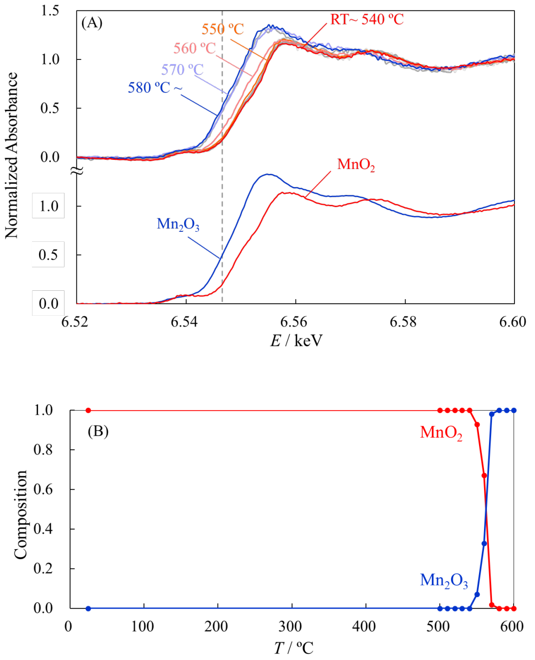

Fig. 5. The change of XANES spectrum (A) and the mole fraction of the Mn species (B) during the heating process at 10 vol% O_2.

up to temperatures approximately 70 °C higher.

The results of *in situ* XAFS analysis when the O_2 content was further increased to 5 vol% and 10 vol% are shown in Figs. 4 and 5, respectively. In the former case, the MnO_2 fraction decreased to 0.75 at 540 °C, and the Mn_2O_3 fraction increased to 0.91 at 550 °C, thus the conversion temperature was determined to be 540 °C. In the presence of 10 vol% O_2, MnO_2 changed to Mn_2O_3 between 550 and 570 °C, and the conversion temperature was 560 °C. From a series of measurements in which the O_2 content was systematically changed as shown in Figs. 2 to 5, this study demonstrated that the oxygen emission process of MnO_2 shifted to higher temperatures in response to the O_2 content in the atmosphere.

3.3. Relationship between O_2 content and conversion temperature

In this study, the conversion temperatures of the oxygen emission process of MnO_2 were determined in detail by *in situ* XAFS analysis under various conditions of O_2 content ranging from 0 vol% to 10 vol%. The determined values of the conversion temperature are summarized in Table 1 and are plotted in Fig. 6 as a function of O_2 content in the atmosphere. The conversion temperature shifted sharply to higher temperatures when the O_2 content was in the range of 0 to 2 vol%, indicating that this temperature responds sensitively to the O_2 content.

Table 1. Conversion temperature of oxygen emission process of MnO_2 under the O_2 atmosphere diluted by He.

O_2 content / vol%	Conversion temperature / °C
0	455
1	520
2	545
3	540
4	540
5	540
8	560
10	560

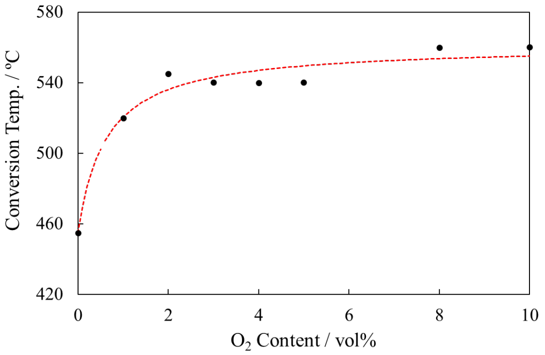

Fig. 6. Conversion temperature of oxygen emission process of MnO_2 as a function of O_2 content. The red broken line represents the empirically reproduced function.

At O_2 contents above 2 vol%, the change in conversion temperature was suppressed, and the conversion temperature with respect to the O_2 content tended to converge to a constant value. When we tried to reproduce the changes shown in Fig. 6 using a general saturation function, we found that the experimental results were empirically reproduced using eq. (2),

$$y = \frac{171\,x}{1+1.61\,x} + 455 \qquad (2)$$

where x and y denote the O_2 content in vol% and the conversion temperature in °C, respectively. In air with an O_2 content of 21 vol%, eq. (2) predicts that the conversion of MnO_2 to Mn_2O_3 occurs at 558 °C. When supported Mn catalysts were prepared by impregnation with an aqueous solution of Mn(II) nitrate, the calcination procedure at temperatures above 560 °C in air resulted in the formation of Mn(III) oxide.

4. Conclusions

In this study, SiO_2-supported MnO_2 catalyst was prepared by drying at 60 °C for more than 5 d using

Mn(II) nitrate as a precursor by the incipient wetness method. *In situ* XAFS analysis for the oxygen emission process of MnO_2 to form Mn_2O_3 was performed under various conditions of O_2 content ranging from 0 vol% to 10 vol%. The conversion temperature shifted to higher temperatures with increasing O_2 content and changed sensitively from 455 °C to 540 °C at O_2 contents below 2 vol%. From the results at a relatively high O_2 content, the conversion temperature in air was predicted to be 560 °C, which is an important insight into the calcination conditions in the synthesis of supported Mn oxide catalysts. These results also suggest new directions for the design and application of Mn-based oxide catalysts to selectively produce an active species by optimizing O_2 content and reaction temperature.

Acknowledgement

The SiO_2 used as the support was that distributed by Catalysis Society of Japan as a reference catalyst.

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