XAFS Analysis for Conversion of Supported Mn Species during Drying Process

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The change in the chemical state of the Mn species supported on SiO₂ and activated carbon (AC) during the drying process was analyzed by means of the XAFS technique. The results revealed that the change of the Mn species differs depending on the supporting material. A single change from the precursor $Mn(NO_3)_2 \cdot 6H_2O$ to MnO₂ was observed on SiO₂, whereas a mixture of $Mn(NO_3)_2 \cdot 6H_2O$, MnO₂, and Mn₂O₃ were appeared on AC and the composition was changed depending on the drying time. It was clarified that the oxidation from $Mn(NO_3)_2 \cdot 6H_2O$ to MnO₂ proceeded for more than 4 days at 60 °C on SiO₂. With prolonged drying, there was a tendency for MnO₂ to decrease and Mn₂O₃ to increase on AC. The oxidation of Mn(NO₃)₂ $\cdot 6H_2O$ to MnO₂ was inhibited, whereas the reduction of MnO₂ to MnO₂ was promoted significantly than on SiO₂.

1. Introduction

Hydrogen generation by electrolysis of water using photovoltaic power generation is one method of generating a sustainable energy source. Electrocatalysts are required for the oxygen evolution reaction, and MnO2 is one of the excellent candidates [1,2]. The MnO₂ species also have an activity for the oxygen reduction reaction which is necessary as electrocatalysts in fuel cells [3-5]. It has also been reported that it can be used as an electrode catalyst in metal-air batteries [6] and as an electrode active material in Zn ion batteries [7]. These functions should be affected by changes in the chemical state of MnO₂. Changes in the chemical state of MnO₂, *i.e.*, a redox reaction between MnO₂ and the Mn(III) state, have been used as an active material of the positive electrode for primary batteries for a long time [8].

Mn oxide is active in the oxidative decomposition of environmental pollutants and is attracting attention from the viewpoint of environmental purification function. The effect of the particle shape of MnO₂ on the oxidative decomposition activity of toluene has been reported [9,10]. There have been reported on the decomposition activity of organic compounds due to differences in the crystal structure of MnO₂ [11]. The selective catalytic reduction of NO_x with NH_3 using the Mn-based oxide catalysts is well known, and its relationship with the oxidation state of the Mn species has been widely discussed [12-15]. The removal of volatile organic compounds (VOCs) is an important issue, and the catalytic oxidation is one of the effective techniques that can convert pollutants into harmless CO₂ and H₂O. The activity of various Mn-based oxide catalysts for catalytic oxidation of VOCs has been intensively studied [16-22], and investigations are currently underway to simultaneous removal of multiple VOCs [16]. 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 facet of the

 MnO_2 catalyst. Reduction of MnO_2 to Mn_2O_3 or Mn_3O_4 changes the catalysis activity [21]. It is considered that the O vacancies on the particle surface can contribute to the catalytic activity for the VOC decomposition, rather than an obvious change in the valence of the Mn center [23].

Changes in the chemical state of Mn oxides have long been the subject of research from the perspective of their catalytic applications. The thermochemical conversion of MnO2 to MnO has been analyzed in several gas atmospheres, and intermediate products of Mn₅O₈, Mn₂O₃, and Mn₃O₄ have been reported [24]. In a study on the possibility of dry reforming of methane by Mn oxide, it has been reported that MnO formed by reduction with methane is oxidized to Mn₂O₃ at 823 K, whereas Mn₃O₄ is generated at 1073 K [25], indicating the self-reduction at high temperature. The variations in the oxidation state have been pointed out for catalyst materials supporting Mn oxide. The influence of the Mn(II) salt used in the synthesis on the oxidation state has been investigated, and it has been reported that Mn₂O₃ and Mn₃O₄ are produced depending on the conditions in addition to MnO₂ [26.27]. Catalytic performance is determined by the chemical state of the generated Mn oxide, and the Mars-Van Krevelen mechanism with the Mn⁴⁺/Mn³⁺ pair is highly active as an oxidation catalysis such as VOC decomposition.

When synthesizing a supported Mn catalyst using the most common impregnation technique, the first step is to impregnate the powder of a supporting material with an aqueous solution of a Mn(II) salt and dry it. In this study, we aimed to analyze the chemical state of the Mn species in a dried sample synthesized using silica and activated carbon (AC) as the supporting material and Mn(II) nitrate as the precursor. The XAFS analysis was carried out with varying drying days. The drying temperature was $60 \ ^{\circ}C$ (silica) or $70 \ ^{\circ}C$ (AC), which can be considered the mildest condition for the calcination process. This study provides basic knowledge for synthesizing the Mn-based oxide catalysts by controlling the oxidation state of Mn.

2. Experimental

Sample Preparation

The powder samples of Mn(II) nitrate supported on SiO₂ (JRC-SIO-10) or AC were prepared by an incipient wetness impregnation method. Mn(NO₃)₂·6H₂O (Fujifilm Wako Pure Chemical) were used as precursors. An aqueous solution of Mn(II) nitrate was added to SiO₂ or AC and dried at 60 °C for 1 d (SiO₂) or 70 °C for 12 h (AC) under air. A portion of the sample powder was removed each day and dried for a total of 8 d (SiO₂) or 10 d (AC) to change the drying time. The Mn loading was 20 wt%(SiO₂) or 40 wt%(AC) in terms of MnO₂.

XAFS measurements

The XAFS measurements were carried out at the Mn K edge in transmission mode using a Si(220) double-crystal monochromators at BL-3 of the SR Center (Ritsumeikan Univ.) and BL-9C of the Photon Factory (KEK). The amount of sample required for the XAFS measurement was estimated based on the absorption coefficient and the tablet was prepared with a diameter of 10 mm by mixing with BN powder.

The linear combination fitting (LCF) analysis was performed using the observed XANES spectrum to determine the sample composition.

3. Results and Discussion

3.1. Mn K-edge XANES

Figure 1 shows the XANES spectra of samples prepared with different drying days supported on SiO₂ and AC. Both supports commonly showed an XANES spectrum with a peak at 6.550 keV when the drying time is short (less than ca. 4 days), but the absorption edge shifted to higher energy as the drying time become longer. The white line peak observed at 6.550 keV is consistent with that of Mn(NO₃)₂·6H₂O. It was found that Mn(II) ions existing in the hexahydrate state in the aqueous solution were directly supported on SiO₂ with nitrate ions as counter ions. For SiO2 samples which was dried for 1 day, the white line peak showed a shoulder on the low energy side, possibly because excess H₂O molecules adsorbed on the SiO₂ surface affected the local structure around the Mn(II) center. When supported on AC, the XANES spectra of samples with a drying time of 1-2 days are not consistent with that of Mn(NO₃)₂·6H₂O. The absorption edge is slightly shifted to the high energy side, and the white line peak is lower. Although the Mn(II) species still exist according to the absorption edge, it is considered that the species with higher valences are mixed.

For both samples with different supports, the



Fig. 1. XANES spectra measured at Mn K edge of samples prepared with different drying days supported on SiO₂ (A) and AC (B). Those of reference samples, $Mn(NO_3)_2 \cdot 6H_2O$, MnO_2 , Mn_2O_3 , and Mn_3O_4 are shown for comparison.

chemical state clearly changes when dried at 60 °C or 70 °C for a long time. The spectrum changed drastically from day 4 to day 5 on SiO₂ and shifted to the spectrum that closely matched MnO₂ with the white line peak at 6.558 keV. It is known that in the general preparation method of supported Mn catalyst using Mn(II) nitrate as a precursor, it is oxidized to MnO₂ during the calcination process in air (e.g., 500 degrees) after the drying process at less than 100 °C [26,27]. In this study, it was revealed that oxidation by nitrate ions to MnO₂ progresses even at a low temperature of 60 °C when kept for more than 5 days.

Such changes are more modest on AC, and the XANES spectrum after 10 days does not completely match that of MnO_2 , as discussed later. However, the absorption edge energy shifts to higher energy, and the white line appears at 6.558 keV, which is similar to the case of SiO₂. The shoulder structure at 6.552 keV seen in the XANES spectrum on day 10 suggests a mixture of oxides with lower oxidation state than MnO_2 . It indicates that some of Mn(IV) oxides are converted to Mn(III) or Mn(II) species during a long drying process.

3.2. Drying process on SiO₂

As mentioned above, in a sample using SiO₂ as the supporting material, the Mn species is supported as Mn(NO₃)₂·6H₂O at the initial stage of drying. This is supported by the comparison of the XANES spectra shown in Fig. 2(A). The XANES spectrum of the sample dried at 60 °C for 6 days shows a prepeak at 6.539 keV, a white line peak at 6.558 keV, and a second peak at 6.575 keV, which are perfectly in accordance with those seen in the spectrum of the MnO₂ standard sample (see Fig. 2(B)). Several isosbestic points are observed in the XANES spectral



Fig. 2. XANES spectrum measured at Mn K edge for the sample supported on SiO_2 dried for 2 days (A) and 6 days (B) compared with that of Mn(NO₃)₂·6H₂O and MnO₂, respectively.

change during the drying process for up to 8 days, as shown in Fig. 1(A). It suggests that the conversion of $Mn(NO_3)_2 \cdot 6H_2O$ to MnO_2 is described by the composition change of the two components. The composition change of the Mn species on SiO₂ was determined by the LCF analysis for the observed XANES spectra using those of $Mn(NO_3)_2 \cdot 6H_2O$ and MnO_2 as the standard spectra. The mole fraction of the Mn species is given in Fig. 3 as a function of drying days. It was found that the oxidation of the Mn(II) center progressed after the 3rd day and quantitatively changed to MnO_2 on the 5th day. The conversion rate is for a sample impregnated on SiO₂ at the loading of 20 wt% and dried at 60 °C, and it



Fig. 3. Change in mole fraction of the Mn species during the drying process on SiO_2 at 60 °C.

may change depending on the loading condition and drying temperature.

3.3. Drying process on AC

In the XANES spectral change during the drying process on AC shown in Fig. 1(B), both the initial and final states are not consistent with the XANES spectrum of the standard compound. Because an aqueous solution of Mn(II) nitrate was used as the precursor, there is a high possibility that Mn(NO₃)₂·6H₂O is supported on AC. In the case of SiO_2 mentioned above, $Mn(NO_3)_2 \cdot 6H_2O$ was converted to MnO_2 , thus it is possible that MnO_2 coexists on AC as well. Figure 4(A) shows a comparison of the spectra obtained after a drying period of 2 days with the results of the LCF analysis using two reference spectra of Mn(NO₃)₂·6H₂O and MnO₂. The calculated spectrum depicted in considering the result of the LCF analysis, 58% of $Mn(NO_3)_2$ ·6H₂O and 42% of MnO₂, agreed well with the observed spectrum. The white line intensity at the early stage of drying is lower than that for SiO₂, which can be interpreted as the oxidation of



Fig. 4. XANES spectrum measured at Mn K edge for the sample supported on AC dried for 2 days (A) and 4 days (B) compared with the results of the LCF analysis using the XANES spectra of $Mn(NO_3)_2 \cdot 6H_2O$ (a), MnO_2 (b), and Mn_2O_3 (c). The red line is the sum of the spectra of the standard compounds represented by gray lines.

 $Mn(NO_3)_2 \cdot 6H_2O$ to MnO_2 progressing within one day.

The white line intensity decreased further after 3 days. The spectrum after 10 days was similar to that of MnO2 but was clearly different in terms of the shoulder structure at 6.552 keV (see Fig. 1(B)). In order to identify the Mn species present, the observed XANES spectrum was compared with the spectra of standard materials (Mn(NO₃)₂·6H₂O, MnO₂, Mn₂O₃, and Mn₃O₄) composed in various combinations. The observed spectrum was well reproduced by adding Mn₂O₃ to Mn(NO₃)₂·6H₂O and MnO₂, as shown in Fig. 4(B). It has been reported that MnO₂ is reduced (deoxygenated) to Mn_2O_3 even under the O_2 atmosphere at high temperature [21,24,25]. It is surprising that the reduction of MnO₂ to Mn₂O₃ progresses during the drying process at 70 °C.

The composition change of the Mn species on AC was evaluated by the LCF analysis of the observed XANES spectra using those of Mn(NO₃)₂·6H₂O, MnO₂, and Mn₂O₃ as the standard spectra. The change was shown in Fig. 5 versus drying days. At the early stage of drying, it existed as a mixture of Mn(NO₃)₂·6H₂O and MnO₂, and the oxidation at room temperature, which was also observed on SiO₂, proceeded rapidly on AC. When the drying time exceeded 3 days, the proportion of Mn₂O₃ gradually increased to replace the decreasing proportion of $Mn(NO_3)_2 \cdot 6H_2O$. MnO_2 tends to increase at the early stage and decrease after 3 days, although the change is minor, indicating that Mn(NO₃)₂·6H₂O is first oxidized to MnO₂ and then reduced to Mn₂O₃. Approximately 20% of Mn(NO₃)₂·6H₂O remained after 10 days of drying, and thus oxidation to MnO₂ was inhibited. On the other hand, the reduction of MnO₂ to Mn₂O₃ was promoted significantly than on SiO₂. These phenomena may be related to the reducing ability of the supporting carbon.



Fig. 5. Change in mole fraction of the Mn species during the drying process on AC at 70 °C.

4. Conclusions

In this study, after being supported on SiO₂ and AC by an impregnation method using an aqueous solution of Mn(II) nitrate, the chemical state changes of the Mn species were analyzed using the XAFS method during the drying process at 60 °C and 70 °C, respectively. It was revealed on SiO₂ that after being supported as Mn(NO₃)₂·6H₂O, it was quantitatively converted to MnO₂ by drying for more than 4 days even at 60 °C. On AC, it was initially supported as $Mn(NO_3)_2 \cdot 6H_2O$, but it was changed to a mixed state of MnO₂ and Mn₂O₃. A clear difference appeared in the supported Mn species between SiO₂ and AC. Fundamental information was obtained for the application of each material, in the case of SiO2 as a supported Mn catalyst and in the case of AC as an electrode active material.

Acknowledgement

The XAFS measurements at the Photon Factory (KEK) were performed under the approval of the Photon Factory Program Advisory Committee (Proposal No. 2023G561).

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