Mem. SR Center Ritsumeikan Univ. No. 25, 28 (2023)

In-Situ XAFS Analysis for Self-Reduction Process of Manganese Oxide on SiO_2

Misato Katayama, Megumi Yoneyama, and Yasuhiro Inada
Department of Applied Chemistry, Faculty of Life Sciences, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu 525-8577, Japan

Manganese oxide catalysts are attracting attention for their ability to purify harmful gases. MnO_2 is known to exhibit high activity at low temperature for the selective reduction of NO using ammonia [1]. In addition, manganese oxide catalysts are also active in oxidation reactions of aromatic hydrocarbons [2]. Chemical species with different oxidation numbers exist stably in manganese oxides, and the catalytic activity varies greatly depending on the oxidation state. Manganese oxide catalysts are generally synthesized by impregnating a stable oxide support with a manganese precursor salt, followed by a calcination treatment under various conditions. It is known that the oxidation state of supported manganese oxide depends on the type of precursor salt and support used. Manganese oxides are known to deoxidize at high temperatures, and the atmosphere and temperature of the calcination process also greatly affect the oxidation state of the manganese species. In this study, we have aimed to analyze the deoxidation reaction of manganese oxide supported on silica at elevated temperatures using *in-situ* XAFS method. The information obtained in this study is important for the proper preparation of the desired manganese oxides supported on silica.

Manganese(II) precursors were supported on silica by the incipient wetness impregnation method using an aqueous solution of manganese(II) nitrate. The sample was dried at 60 ˚C in air and subjected to *in-situ* XAFS measurements of the temperature-programmed deoxygenation process. The XAFS measurements at the Mn K-edge were carried out at BL-3 of the SR Center in the transmission mode under a He-diluted O_2 gas flow (10 vol%) at elevated temperatures to 700 °C.

Fig. 1 shows the XANES spectra measured for samples with two loadings of the Mn species. The spectrum before the temperature rise was almost the same as that of MnO_2, and it was found that manganese(II) nitrate impregnated into silica was oxidized to MnO_2 by drying at 60 °C. MnO_2 was maintained in the temperature range up to 500 °C, and it was revealed that the spectrum was changed to that similar to Mn_2O_3 by heating up to 700 °C. Figure 2 shows a plot of the X-ray absorbance at 6550 eV as a function of temperature. The absorbance clearly changed from 500 °C to 600 °C, and the temperature, at which MnO_2 deoxygenated to form Mn_2O_3 under an oxygen atmosphere, was determined by *in-situ* XAFS measurements, and it was clarified that the temperature does not depend on the Mn loading.

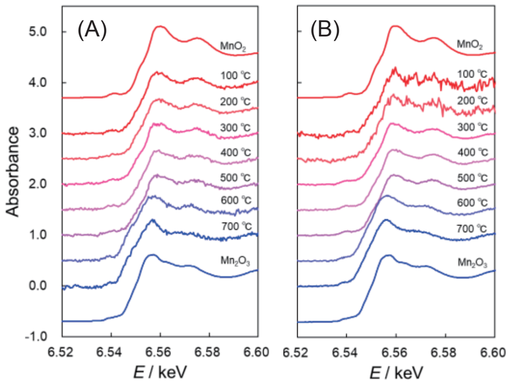

Fig. 1 Observed XANES spectra during the heating process under a He-diluted O_2 gas flow for the samples with the Mn loading of 3 wt% (A) and 10 wt% (B).

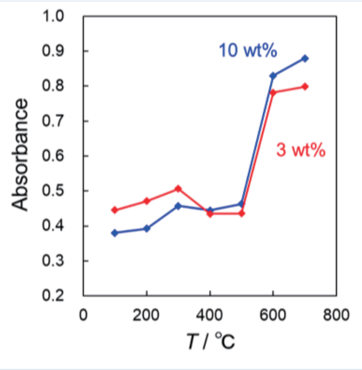

Fig. 2 X-ray absorbance change as a function of temperature at 6550 eV.

References

[1] J. Li, H. Chang, L. Ma, J. Ma, J. Hao and R. T. Yang, *Catal. Today*, **2011**, *175*, 147-156.
[2] H. Einaga, S. Yamamoto, N. Maeda and Y. Teraoka, *Catal. Today*, **2015**, *242*, 287-293.