In situ XAFS Analysis for Calcination Process Under Hydrogen Atmosphere of Manganese Chloride Supported on Active Carbon

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Supported metal catalysts using precious metals are widely used in the chemical industry, but the development of catalysts using base metals as alternative materials has been attracting attention, mainly from the perspective of cost [1,2]. Research and development into the improvement of performance of supported catalysts using Mn, a type of base metal, is being continuously conducted, and it is important to understand the chemical state of the Mn species during the preparation process. In this study, Mn catalyst supported on activated carbon (AC) was prepared by the impregnation method using an aqueous solution of $MnCl_2 \cdot 4H_2O$, and *in situ* XAFS analysis was performed during the calcination process. We clarified the chemical state change of the supported Mn species under a H_2 atmosphere.

An aqueous solution of $MnCl_2$ was added dropwise to the AC powder, and the mixture was dried at 50 °C for 12 h. *In situ* XAFS measurements were performed up to 700 °C under a H_2 gas flow diluted by He (10 vol%) at BL-3 of the SR Center (Ritsumeikan Univ.).

The observed XANES spectral change is shown in Fig. 1 together with the spectra of standard samples. By switching from air to H_2 gas flow, the white line peak shifted to lower energy, and the absorbance of the white line peak around 6.547 keV decreased with increasing temperature. The white line peak shifted to higher energy in the temperature range from 500 °C to 600 °C. The XANES spectrum, which became constant above 600 °C, was consistent with that of MnO. Figure 2 shows the change in absorbance versus temperature at two characteristic energies where the absorbance changed significantly. At both energies, the absorbance dropped sharply when switching from air to H_2 gas flow at room temperature and then increased sharply from 500 °C to 600 °C. The latter corresponds to the conversion to MnO, and the observed change in the sample mass before and after this conversion revealed that Mn_2OCl_2 was generated at around 150 °C. Since the absorbance remained nearly constant between 150 °C and 450 °C, the species present up to 450 °C is presumed to be Mn_2OCl_2. The spectral change below 100 °C is thought to correspond to the dehydration of supported $MnCl_2$ hydrate, but it does not change to a completely anhydrous form, and it is considered that the Mn(II) oxychloride is formed accompanied by decomposition of the hydrated water. In this study, we clarified the conversion to MnO via Mn_2OCl_2 during the calcination process under an H_2 atmosphere, but this fact is expected to be highly dependent on the gas environment.

References

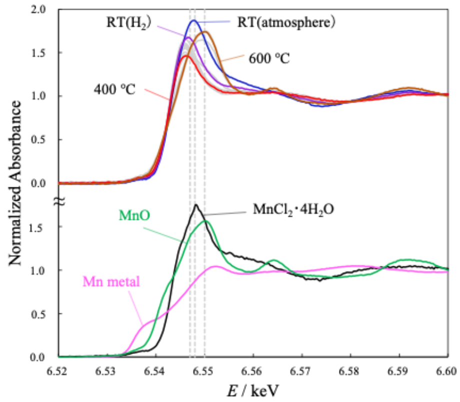

Fig. 1. XANES spectral change of $MnCl_2$/AC during the calcination process under diluted H_2 atmosphete.

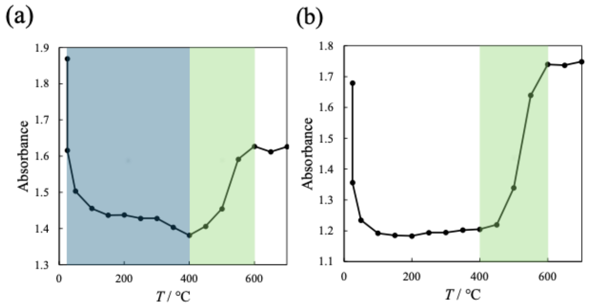

Fig. 2. The plots of absorbance at 6.548 keV (a) and 6.550 keV (b) versus temperature.

[1] J. Li, X. Liang, S. Xu, and J. Hao, *Appl. Catal. B*, **90**, 307 (2009).
[2] J. Lou, H. W. Yang, and C. H. Lin, *Aerosol Air Qual. Res.*, **9**, 435 (2009).