# Chemical State Analysis for Calcination Process of $SiO_2$-Supported Chromium Catalyst

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Chromium oxides, which have a variety of oxidation states, are used in many catalysis reactions, and the knowledge of their chemical states is essential to understanding their catalytic activity. Supported chromium catalysts have been applied in numerous chemical reactions, including ethylene polymerization, alkane dehydrogenation, and oxidative dehydrogenation, as well as selective oxidation reactions [1]. In this study, $SiO_2$-supported chromium catalyst was prepared by the impregnation method, and *in situ* XAFS analysis was carried out on the preparation process.

Silica powder was suspended in an aqueous solution of chromium nitrate acidified with nitric acid and dried in air at 120 °C for 12 h. The obtained powder was subjected to the calcination up to 700 °C under a flow of $O_2$ gas diluted with He (10 vol%), and *in situ* XAFS measurements were performed at the Cr K edge at BL-3 in the SR Center (Ritsumeikan Univ.).

To analyze the chemical state in the initial samples, the linear combination fitting (LCF) analysis was applied to the XANES spectrum obtained at room temperature using $CrO_3$ and $Cr(NO_3)_3{\bullet}9H_2O$ as reference samples. The measured spectrum was well reproduced as a mixture of 53% $CrO_3$ and 47% $Cr(NO_3)_3{\bullet}9H_2O$ as shown in Fig. 1. It was clarified that a significant amount of the Cr(III) precursor was oxidized to Cr(VI) during drying at 120 °C for 12 h. The Fourier transform function obtained from the EXAFS spectrum of this sample is shown in Fig. 2 together with those of reference samples. The main peak observed at 1.7 Å is almost identical to that of $Cr(NO_3)_3{\bullet}9H_2O$, but the shoulder structure at around 1.3 Å supports the coexistence of $CrO_3$.

Figure 3 shows the change in the XANES spectrum obtained by *in situ* XAFS measurement during the calcination process in which the temperature was raised to 700 °C under a 10 vol% $O_2$ flow. The spectra were almost the same below 400 °C, and the composition of the mixture was almost constant. A significant change was observed between 400 °C and 500 °C, in which the intensity of the pre-edge peak decreased, and the absorption edge shifted to lower energy. The spectrum was constant above 500 °C, which agreed well with that of $Cr_2O_3$. This study revealed that the Cr(VI) species presented at temperatures below 400 °C were reduced even in an $O_2$ atmosphere, producing $Cr_2O_3$ by the calcination at 500 °C or higher. This study provides important information for the preparation of catalysts using Cr(III) nitrate as a precursor.

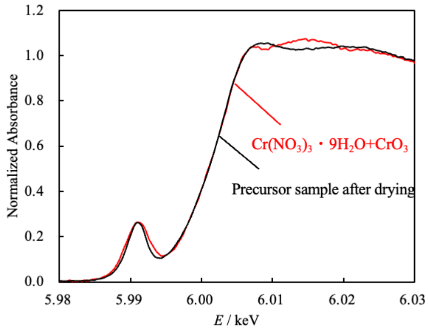

**Fig. 1.** XANES spectrum of the sample before calcination and its LCF analysis result.

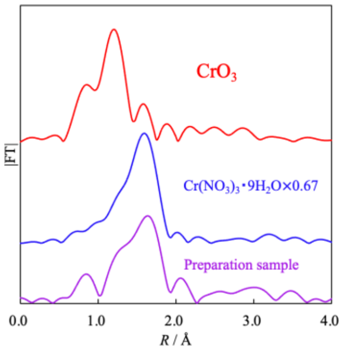

**Fig. 2.** Fourier transform functions of the sample before calcination and standard samples.

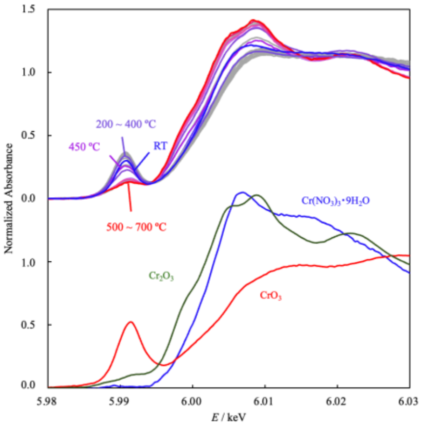

**Fig. 3.** XANES spectral change during calcination process up to 700 °C.

## Reference

[1] J. Handzlik, R. Grybos, and F. Tielens, *J. Phys. Chem. C*, **2016**, *120*, 17594.