## Chemical State Analysis of Dehydration Process of FeCl<sub>3</sub>•6H<sub>2</sub>O Supported on Silica

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Iron, which is abundant in the environment, is cost-effective as a catalyst material. It is well known that the iron species supported on stable oxides are catalytically active in ammonia synthesis by the Haber-Bosch process, as well as in the Fischer-Tropsch synthesis [1] and the water-gas shift reaction [2], and thus it is important to reduce the cost of the synthesis process. Various iron compounds are used in the synthesis of supported iron catalysts, one of which is iron(III) chloride hydrate. When synthesized by impregnation with an aqueous solution of iron(III) chloride, it is initially supported as a hydrate. The desired iron species can be obtained by treating at the elevated temperature under various conditions. Knowing the changes in the chemical state of the iron species during the synthesis process is important information for selectively obtaining the target iron species. In this study, the heating process of iron(III) chloride hydrate supported on silica under an H<sub>2</sub> gas flow was analyzed using in situ XAFS and thermogravimetry-differential thermal analysis (TG-DTA) measurements.

The SiO<sub>2</sub> (JRC-SIO-10) powder was impregnated with an aqueous FeCl<sub>3</sub> solution under an incipient wetness condition. The mixture was dried at 60 °C for 6 h. The loading of FeCl<sub>3</sub> hydrate was determined to 32 wt% by the X-ray fluorescence analysis. *In situ* XAFS measurements at the Fe K edge of the obtained sample during the heating process in a He diluted H<sub>2</sub> gas (10 vol%) atmosphere were carried out at BL-3 (SR Center) and BL-9C (KEK-PF).

Figure 1 shows the XANES change in the temperature range up to 135 °C. The initial spectrum



Fig. 1. Changes in XANES spectra at the Fe K edge during the TPR process in the temperature range from 30  $^{\circ}$ C to 135  $^{\circ}$ C.

is consistent with that of FeCl<sub>3</sub>•6H<sub>2</sub>O. When the temperature was increased in a dry atmosphere, the shoulder structure around 7.120 keV became clear, and the peak intensity from 7.126 keV to 7.135 keV decreased. The XANES spectrum at 135 °C differs from that of FeCl<sub>2</sub>•4H<sub>2</sub>O, and it is obvious that the Fe center remains in the oxidation state of +3. According to the TG-DTA results shown in Fig. 2, a weight loss of 2.3 mg was observed between 50 °C and 120 °C, which corresponds to 6 equivalents of H<sub>2</sub>O relative to Fe. Therefore, it is concluded that the XANES spectrum observed at around 135 °C corresponds to that of FeCl<sub>3</sub> anhydride. Because the Fe(III) ion is surrounded by six chloride ions in an octahedral configuration for anhydrous FeCl<sub>3</sub> [3], this study showed that the substitution of water with chloride ions extends the absorption edge to the lower energy and reduces the intensity of the white line.



**Fig. 2.** Curves of thermogravimetric analysis (a) and differential thermal analysis (b) in the temperature range up to  $200 \,^{\circ}$ C.

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## References

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