Development of *In-Situ* XAFS Cell for Fluorescence Yield Detection and Application to Dilute Heterogeneous Catalysts

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1. Introduction

The particle surface of active metal catalysts is known to be a reaction field of heterogeneous catalysts. The enhancement of the surface area leads to the activation improvement, and thus a great effort has been made to refine the supported metal species. A dilution of metal species is one of ways to achieve the refinement. Therefore, the establishment of the analysis technique for such dilute heterogeneous catalysts is very important to know the electronic and structural aspects. In this study, we have developed an *in-situ* XAFS cell for the fluorescence yield detection, because the conventional *in-situ* cell is used only in the transmission mode and its application to dilute samples is impossible. This is a first report to show the XAFS spectra of dilute Ni catalysts supported on SiO_2 under a reactive gas environment at elevated temperature.

2. Cell Development

The schematic draw of the developed *in-situ* cell is shown in Fig. 1. The powder sample is mounted in an SUS ring, which is placed with the angle of 45 ˚ against the incident X-ray. The fluorescent X-rays emitted from the sample is detected using an SSD with the acceptance angle of 10 ˚. The cell body is heated using four cartridge heaters, and the applicable highest temperature is about 800 ˚C. Because the cell body and the sample holder are made of stainless steal, the fluorescence contaminations

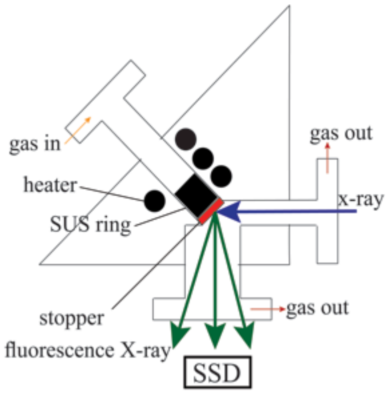

Fig. 1. Schematic draw of developed *in-situ* XAFS cell for fluorescence yield detection.

should be carefully checked.

3. Results and Discussion

The *in-situ* XAFS measurements of Ni catalysts (0.5 and 10 wt%) were carried out at BL-3 of SR Center in Ritsumeikan University under the diluted H_2 gas flow (10 vol% with He, 200 cm^3/min) up to 600 ˚C.

The observed XANES change for the reduction process of supported NiO by H_2 is shown in Fig. 2 together with that for a standard Ni loading (10 wt%). The self-absorption effect diminishes the fluorescence intensity at the white line of NiO for the concentrated sample. The clear XANES change from NiO to Ni(0) metal is appeared for both samples with the different Ni loading, indicating that the developed *in-situ* cell works correctly. In addition, the operand XAFS observation in the fluorescence mode has been first succeeded for dilute Ni catalysts.

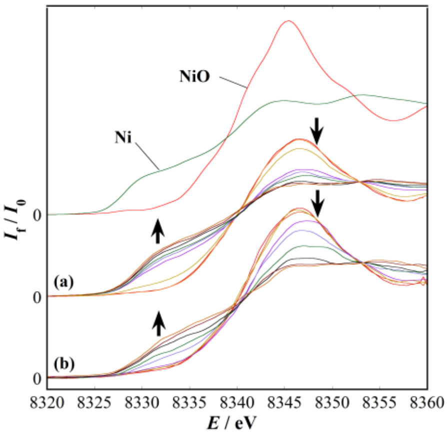

Fig. 2. XANES change for reduction of supported NiO species with the loading of 10 wt% (a) and 0.5 wt% (b).

Figure 3 shows the temperature dependence of the observed fluorescence intensity normalized by I_0 as a function of temperature. The rapid decrease at around 350 ˚C corresponds to the reduction of NiO. The temperature dependences for the concentrated sample are consistent for two types of detection. In contrast, the reduction temperature for the diluted catalyst is found to be slightly higher than that for the concentrated sample. A recent research of reduction for the supported Ni catalysts shows the independent temperature dependence in the concentration range from 5 to 15 wt% [1]. The developed *in-situ* cell has first revealed that the reduction of supported NiO species is restrained for the diluted catalyst. The dispersion of supported Ni species may contribute to the relative stability of NiO.

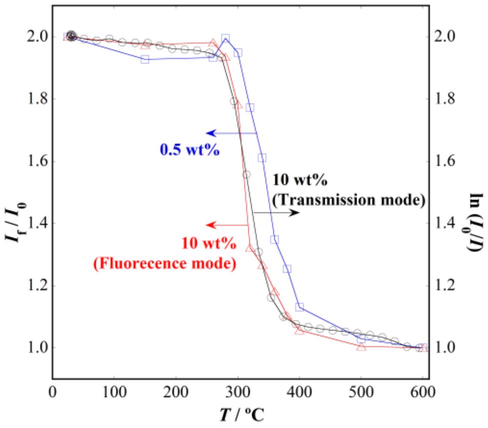

Fig. 3. Temperature dependence of normalized fluorescence intensity at 8347 eV as a function of temperature.

Reference

[1] S. Yamashita, M. Katayama, and Y. Inada, *J. Phys. Conf. Ser.*, **430**, 012051 (2013).