Development of *In-Situ* XAFS Cell for Characterization of Catalysts Using Conversion Electron Yield Detection

Toshiki Watanabe, Shohei Yamashita, Misaki Katayama,
and Yasuhiro Inada

Department of Applied Chemistry, Graduate School of Life Sciences, Ritsumeikan University,
1-1-1 Noji-Higashi, Kusatsu, Shiga 525-8577, Japan.

1. Introduction

The heterogeneous catalysts utilize for various purposes and the functions are usually produced by rare metal elements, such as Pt, Rh, and Pd. The alternative materials with at least same performance are necessary to maintain and improve the human society. To achieve the development of new catalysis systems without rate metal elements, it is very important to characterize the supported active metal species in various heterogeneous catalysts. X-Ray absorption fine structure (XAFS) is a powerful technique to analyze the oxidation state and local structure of metal species. There are some types to measure the XAFS spectrum, and the transmission mode is the most fundamental type, for which the incident and transmitted intensities are simultaneously measured. However, the X-ray transmission through the sample is required to apply the transmission mode. The fluorescence yield and the electron yield are alternatively used when the transmission measurements are impossible. The conversion electron yield (CEY) measurement is also useful for such cases. The surface sensitivity and the applicability under the ambient conditions are the great advantage to the fluorescence and the normal electron yield detection, respectively. The information of surface species of the catalyst particle is very important to understand the characteristics of heterogeneous catalysts. Because the CEY measurements are usually carried out under He gas flow condition, the CEY technique has a possibility to achieve under the reaction conditions of heterogeneous catalysts. In this study, the *in-situ* XAFS cell for the CEY detection has been developed to achieve the XAFS measurements under the reaction gas flow at elevated temperature.

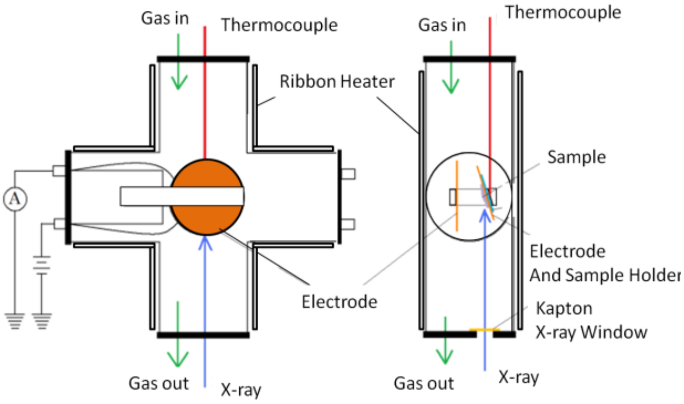

Fig. 1. A schematic draw of developed in-situ cell for CEY detection.

2. Experimental

A design of the newly developed cell for the in-situ CEY measurements is schematically shown in Fig. 1. The cross tube with NW-16 quick couplings was used as the cell body. The sample is put on a sample electrode made of copper. The bias voltage (*ca.* 200 V) is applied with a counter electrode. A ceramics plate heater set under the sample electrode is used to heat the sample.

The XAFS measurements were carried out at BL-3 of the SR center in Ritsumeikan University and at BL-12C of Photon Factory in KEK. The Ni K-edge measurements were performed for NiO/α-Al_2O_3 (10 wt%) under the flow of diluted H_2 gas (20 vol%) balanced with He. The Fe K-edge spectra were recorded for Fe_2O_3 powder at elevated temperature.

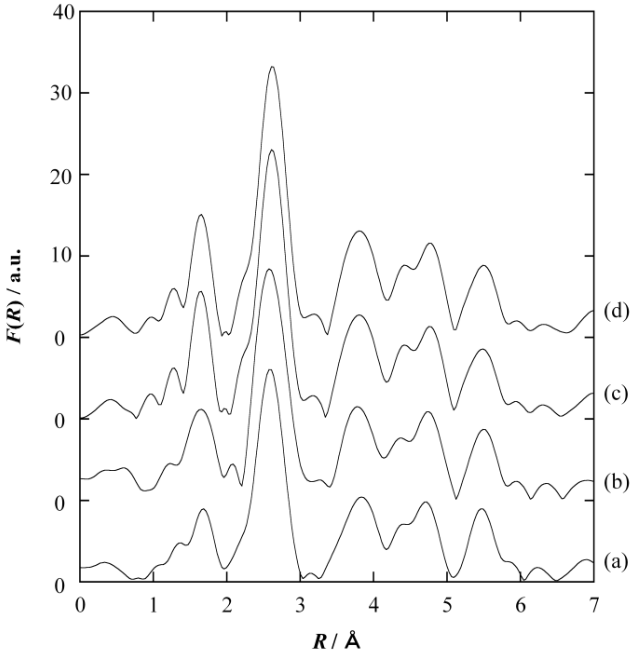

Fig. 2. Radial structure functions, |*F*(*R*)|, for the standard sample of NiO (a), and NiO/α-Al_2O_3 measured by the transmission mode (b) and by the CEY mode under H_2 gas-flow (c and d). The

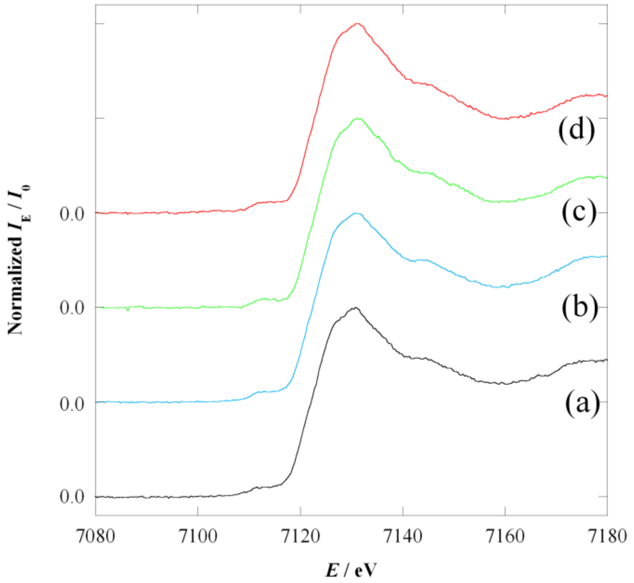

Fig. 3. XANES spectra of Fe_2O_3 measured at 298 K (a), 341 K (b), 402 K (c), and 420 K (d).

3. Results and Discussion

Radial structure functions, |*F*(*R*)|, of NiO/α-Al_2O_3 are shown in Fig. 2, in which the results of the CEY detection are compared with that of the transmission measurement. Figure 2 clearly shows that the functions obtained by the CEY measurement under H_2 are perfectly in agreement with that obtained by the transmission mode. It is thus confirmed that the developed CEY cell is applicable to the H_2 gas condition. Although the NiO/α-Al_2O_3 powder was kept for 30 min under the H_2 gas flow, the local structure around the Ni atom was not changed. It is found that the surface NiO species of the supported particle on α-Al_2O_3 is not reduced at room temperature.

The XANES spectra of Fe_2O_3 are given in Fig. 3. All spectra are perfectly in consistent, indicating that the developed

CEY cell is possible to be used up to at least 420 K. Because of the use of an electronically insulating material, which is melt at 538 K, the maximum temperature of the present CEY cell is about 500 K.

In the future, we will develop the next version of the *in-situ* CEY cell, which will increase the temperature limit. The *in-situ* CEY cell will be applied to the surface-sensitive XAFS measurements for heterogeneous catalysts under the reaction conditions.