XAFS Analysis on Preparation Processes of FeNi Alloy Catalyst Supported on Silica

Yuki Kondoh, Shohei Yamashita, Misaki Katayama, and Yasuhiro Inada
Department of Applied Chemistry, Faculty of Life Sciences, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu 525-8577, Japan

Ni nanoparticle supported on a stable material is widely used as a catalyst for various reactions such as reforming reactions to generate hydrogen and combustion reactions of hydrocarbons. An addition of other metal element is a potential development to improve the catalytic performance. For the Ni catalysts, the addition of Fe is known to enhance the reforming performance, however the effect of the Fe species is not well understood. The mechanistic clarification of the preparation process is necessary to know the actually existing species under the catalytic reaction conditions. In this study, *in-situ* XAFS analysis has been carried out for the reduction process of the impregnated precursor to prepare the FeNi alloy catalyst.

The FeNi catalyst is normally prepared by the impregnation method. Both of $Ni(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ was dissolved in water, and the SiO_2 powder was suspended into the solution. The mixture was dried at 70 ºC in air, and the obtained powder was subject to the calcination at 600 ºC in air. The *in-situ* XAFS measurements were carried out at both the Fe and Ni K edges for the succeeding temperature-programmed reduction (TPR) process at BL-3 of the SR Center (Ritsumeikan Univ.) and BL-9C of the Photon Factory (KEK). The temperature was increased up to 600 °C with the heating rate of 10 ºC/min under the H_2 gas flow diluted by He (10 vol%). The obtained FeNi alloy catalyst was characterized by the X-ray diffraction (XRD) measurement. The composition of Fe and Ni was determined by the X-ray fluorescence (XRF) analysis to be 4.66 and 5.35 wt% for Fe and Ni, respectively, so that the molar ratio of Ni to Fe was 1.1 : 1.

The Fe species in the impregnated precursor after the calcination was assigned to either or both $NiFe_2O_4$ and Fe_3O_4 by the XRD analysis. This suggested the existence of NiO according to the molar ratio of Fe and Ni. The XRD characterization clearly demonstrated that the FeNi alloy was formed in the final sample after the TPR treatment.

Figure 1 shows the XANES spectral change during the TPR process of the impregnated precursor after the calcination. The initial spectrum at the Fe K edge was identical to that of $NiFe_2O_4$, indicating that almost half of Ni was contained in the mixed metal oxide of $NiFe_2O_4$. The EXAFS analysis also derived the same conclusion for the Fe species. The initial XANES spectrum at the Ni K edge was reasonably reproduced in considering the existence of both $NiFe_2O_4$ and NiO. The molar ratio (Ni/Fe) of 1.1 determine by the XRF analysis concluded the formation of $NiFe_2O_4$ and NiO with the molar ratio of 5 : 6 in the impregnated precursor after the calcination.

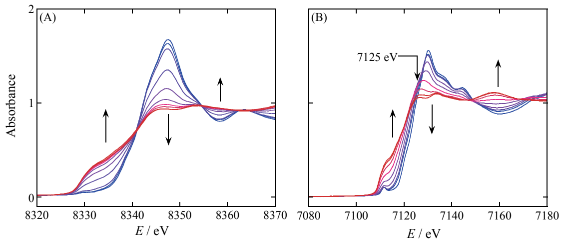

Fig. 1 XANES change measured at the Ni (A) and Fe (B) K edge during the TPR process of the impregnated precursor after the calcination.

The XANES change for the Fe species clearly demonstrated that the intermediate species existed at around 380 ºC during the reduction from $NiFe_2O_4$ to FeNi. All XANES data were used to estimate the component species by the linear combination fitting using some possible reference compounds. The results of the composition analysis are given in Fig. 2. It was found that the $NiFe_2O_4$ species was first reduced to the intermediate FeO at above 150 ºC, and the Ni species was then separated as NiO.

$$NiFe_2O_4 + H_2 \rightarrow 2FeO + NiO + H_2O \qquad (1)$$

The mixture of FeO and NiO was simultaneously reduced at around 380 ºC to form the final product of the FeNi alloy.

$$NiO + FeO + 2H_2 \rightarrow FeNi + 2H_2O \qquad (2)$$

The present *in-situ* XAFS study successfully clarified the elementally steps during the formation of the FeNi alloy catalyst, and will provide important information to modify the particle size for the performance improvement.

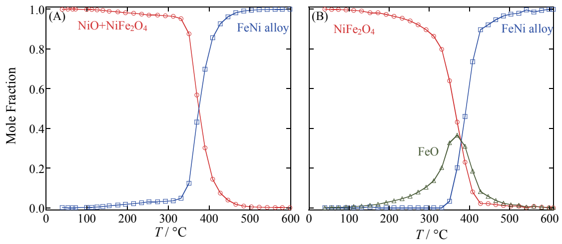

Fig. 2 The composition change for the Ni (A) and Fe (B) species as a function of temperature during the TPR process to prepare the FeNi alloy catalyst.