In-situ XAFS Study on Cobalt-based Catalyst

Yoshimu IWANAMI1,*, Nobuharu KIMURA1, Ken’ichi KIMIIIMA2, Yasuhiro NIWA2, Hitoshi ABE3, and Masao KIMURA2
1 ENEOS Corporation, 8 Chidoricho, Naka-ku, Yokohama, 231–0815, Japan
2 Photon Factory, Institute of Materials Structure Science, High Energy Research Organization, 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan

1 Introduction
Hydrocarbons can be produced from a feed containing CO and H2 using a cobalt-based catalyst (Co catalyst). The Co catalyst can be used in the process for the hydrocarbon production after the activation, i.e. H2 reduction, of the Co catalyst precursor (cobalt oxide).

In this study, we investigated the chemical-state and structural change of the cobalt species on the Co catalyst during the activation process by way of in-situ Co K-edge XAFS measurements to gain a better understanding of the activation process.

2 Experiment
We prepared a silica-supported Co catalyst. In the activation process, cobalt oxides on the catalyst are converted to active species cobalt metals through H2 reduction. The chemical-state and structural changes of the Co species on the catalyst during reduction were observed by way of Co K-edge in-situ XAFS measurements in transmission mode at the BL9C of the Photon Factory. H2 reduction was performed by placing the Co catalyst in an in-situ XAFS cell and heating it at a designated temperature under a flowing H2 atmosphere for two hours. Before the Co catalyst was heated to the target temperature, it was kept under a flowing He atmosphere. Once the temperature reached the target value, the He gas was changed to an H2 gas, and XAFS spectra were collected every 80 seconds.

3 Results and Discussion
The Co K-edge XANES spectra obtained at the designated temperature for the Co catalyst and those of cobalt metal and cobalt oxides are shown in Fig. 1. We found that the shapes of the XANES spectra changed over time during H2 reduction. Before the reduction, i.e., at a reduction time of 0 min, the shape of the XANES spectra of the Co catalyst is very similar to that of Co3O4. At the beginning of the reduction, the shape of the spectra is similar to that of CoO, and thereafter, it is similar to that of the active species cobalt metal. We examined the change of the chemical states of the Co species on the Co catalyst during H2 reduction. The XANES spectra of the Co catalyst were pattern-fitted with those of Co3O4, CoO, and cobalt metal. The ratios of the cobalt species on the Co catalyst are plotted against the reduction time as shown in Fig. 2. The cobalt species changed from Co3O4 to CoO and Co metal rapidly during reduction. After about one minute, Co3O4 disappeared, and the ratio of cobalt metal increased.
gradually as the reduction proceeded. After the 60-minute reduction, the ratio of cobalt metal reached a constant value (about 0.9).

Furthermore, we examined the Fourier transforms (FTs) of EXAFS obtained during H\textsubscript{2} reduction as shown in Fig. 3. We focused on the Co-Co peak originating from cobalt metal, i.e., the active species, on the Co catalyst. We found that the peak height of Co-Co changed over time during H\textsubscript{2} reduction. So, we examined the relationship between the reduction time and the peak height of Co-Co. As a result, we found that the peak height of Co-Co increased rapidly at the beginning of the reduction, and gradually increased and reached an almost constant value after the 60-minute reduction (Fig. 4). This suggests that the cobalt metal particles, which were converted from cobalt oxide, on the Co catalyst would grow larger as the H\textsubscript{2} reduction time increased. However, the particle size would not change after the 60-minute reduction.

* iwanami.yoshimu@eneos.com