C K-edge XANES analysis of coke on CoMo catalysts used in HDS unit using feeds of LGO mixed with heavy fuel oil blendstocks

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1 Introduction

To ensure the most effective use of petroleum resources, efficient techniques must be developed for converting blendstocks of heavy fuel oil to diesel fuel oil. However, when a mixture of light gas oil (LGO) and light cycle oil (LCO), a heavy fuel oil blendstock, is fed into an oil refinery's hydrodesulfurization (HDS) unit to produce diesel fuel, the CoMo (Cobalt-Molybdenum) catalyst in the HDS unit is rapidly deactivated (Fig. 1). In contrast, when the feed is LGO mixed with residue desulfurization gas oil (RDS-GO), another heavy fuel oil blendstock, the catalyst is deactivated slowly. With this in mind, we focused on the coke, or carbonaceous matter, that forms around the active species, namely MoS_2, on the catalyst surface during the HDS reaction and is thought to be the primary cause of deactivation of gas oil HDS catalysts. [1]

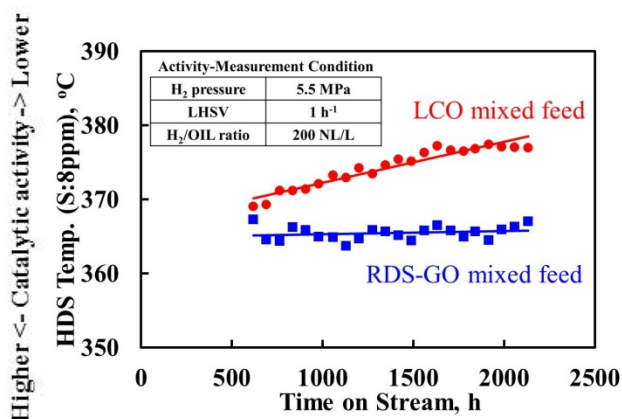In this study, we investigated the chemical states of the

Fig. 1: Deactivation behaviour of catalyst for two different feeds (bench-scale plant).

coke formed on spent CoMo catalysts from an HDS unit by way of C K-edge XANES measurements in order to understand the mechanism of catalyst deactivation when the HDS feed is LGO mixed with heavy fuel oil blendstocks such as LCO and RDS-GO.

2 Experiment

For the C K-edge XAFS measurements, we prepared spent aluminum oxide-supported CoMo catalysts which had been used for 160, 500, 1000 and 2300 hours on stream in the HDS unit of a bench scale plant, using feeds consisting of LGO mixed with 15 vol% of either LCO or RDS-GO. The carbon concentrations in the catalysts used for the LCO-containing mixed feed were around 5–8 mass%, and those used for the RDS-GO-containing mixed feed were around 4–5 mass%.

Before the XANES measurements, the catalysts were subjected to Soxhlet extraction (using toluene) for 12 hours to remove the oil on them and then ground into powders. The powdered catalysts were then fixed on an indium plate, which was mounted on the sample plate that goes in the XAFS instrument. The XANES measurements were conducted in total electron yield mode on station BL-7A at the Photon Factory.

3 Results and Discussion

Figures 2 and 3 show the C K-edge XANES spectra of spent CoMo catalysts used for different times on stream in the HDS unit of a bench scale plant, using LCO-containing mixed feed and RDS-GO-containing mixed feed. Two sharp peaks were observed at 285 eV and around 288 eV and a broad peak was also observed around 292 eV in the XANES spectra of all spent catalysts. The spectra were normalized at the peak around 292 eV. Aromatic compounds and basic nitrogen compounds in the feeds have been reported as potential causes of coking. [2] Therefore, the peak observed at 285 eV was assigned to the 1s $->\pi^*$ transition of the sp^2 carbon atoms in aromatic compounds, and that at around 292 eV was assigned to the 1s $->\sigma^*$ transition. Meanwhile, the peak observed around 288 eV may be due to the alkyl groups in the aromatic compounds or the presence of oxygen-containing or nitrogen-containing functional groups.

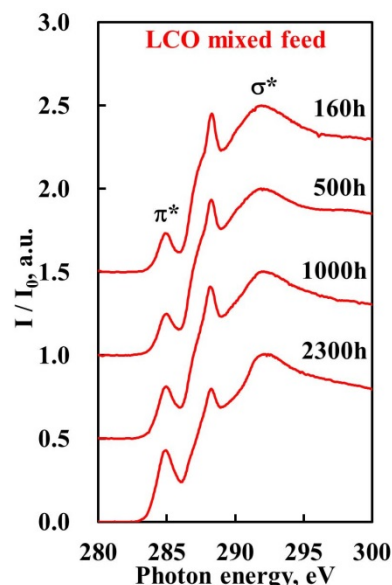It was found that the peak heights of the 1s $->\pi^*$

Fig. 2: C K-edge XANES spectra of spent CoMo catalysts for LCO mixed feed.

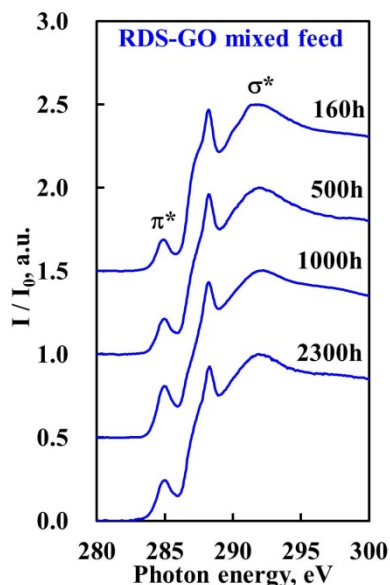transition peaks were clearly different depending on the

Fig. 3: C K-edge XANES spectra of spent CoMo catalysts for RDS-GO mixed feed.

times on stream for the catalysts used with both the LCO-containing mixed feed and RDS-GO-containing mixed feed. Therefore, we focused on the 1s $\rightarrow \pi*$ transition peak at 285 eV in order to elucidate the chemical states of the coke formed on the spent CoMo catalysts during the HDS reaction.

The peak height ratio of the 1s $\rightarrow \pi*$ transition peak to the 1s $\rightarrow \sigma*$ transition peak was determined by the height of each peak. [3] The peak height ratio ($\pi*$ / $\sigma*$) was viewed as a measure of the degree of polycyclization of the aromatic compounds in the coke on the spent catalyst. The higher the peak height ratio ($\pi*$ / $\sigma*$), the higher we expect the degree of polycyclization of the aromatic compounds to be.

The relationship between the time on stream and the peak height ratio ($\pi*$ / $\sigma*$) for the spent catalysts used with the LCO-containing mixed feed and the RDS-GO-containing mixed feed is shown in Fig. 4. Figure 4 shows that the peak height ratio ($\pi*$ / $\sigma*$) increased with the time on stream for the spent catalyst used with the LCO-containing mixed feed. This suggests that the aromatic
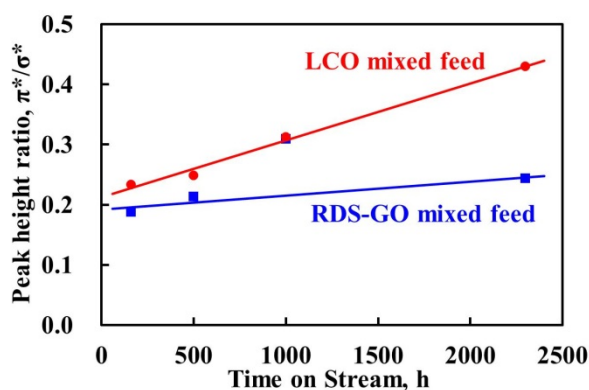

Fig. 4: Relationship between the time on stream and the peak height ratio ($\pi*/\sigma*$) in the XANES of spent catalysts.

compounds in the coke that formed on the catalyst became more polycyclic as the time on stream increased. In contrast, the peak height ratio ($\pi*$ / $\sigma*$) of the catalyst used with the RDS-GO-containing mixed feed increased much less than that of the catalyst used with the LCO-containing mixed feed as the time on stream increased, with the exception of an outlying data point at the 1000-hour mark. This suggests that the aromatic compounds in the coke on the catalyst were less likely to become polycyclic as the time on stream increased.

These results suggest that the chemical state of the coke forming on a catalyst will differ depending on the feed used in the HDS reaction, and this affects the catalyst deactivation behavior.

References
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[2] E. Furimsky et al., Energy Fuel, **9**, 439 (1995).
[3] Y. Muramatsu et al., Advances in X-Ray Chemical Analysis **43**, 425 (2012).

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