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In-situ EXAFS study on a spent CoMo HDS catalyst during regeneration at various temperatures

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Introduction

The hydrodesulfurization (HDS) catalyst used in an oil refinery is deactivated during operation [1]. However, the spent catalyst can be reused after a regeneration process, whereby cokes deposited on the catalyst are removed. From an environmental standpoint, the regeneration of catalysts used in refineries is becoming increasingly important. Researchers must gain a better understanding of the regeneration process, so as to optimize the regeneration conditions, with the goal of wider use of regenerated catalysts.

Previous studies have shown that the HDS activity of regenerated CoMo catalysts vary depending on the regeneration temperature. It was therefore expected that the time required for regeneration would vary depending on the regeneration temperature. In this study, in order to optimize the time required for regeneration, the authors investigated the chemical-state change of the Mo species on the spent catalyst during regeneration by way of *in-situ* Mo K-edge EXAFS measurements.

Experimental

A CoMo/Al_2O_3 catalyst used for two years in the HDS processing of gas oil in a refinery was used for this study. In the regeneration process, active Mo species, i.e. Mo sulfides, on the spent catalyst change to Mo oxides through oxidation. We observed the chemical-state changes of Mo species by way of Mo K-edge *in-situ* EXAFS measurements in transmission mode at NW10A. Regeneration was performed by placing the spent catalyst in an *in-situ* EXAFS cell and heating at three discrete temperatures under a flowing air atmosphere. Before the catalyst was heated to the target temperature, the catalyst was kept under a flowing nitrogen atmosphere. Once the temperature reached the target value, nitrogen gas was changed to air and EXAFS spectra were collected every 1 minute.

Results and Discussion

The Fourier transforms (FTs) of EXAFS obtained at the regeneration temperature, T °C, are shown on the left in Figure 1. The shapes of the FTs of the EXAFS spectra changed over time during regeneration. Thus, we focused our attention on the Mo-S peaks originating from Mo sulfide on the catalyst in the FTs of the EXAFS spectra, and examined the relationship between the regeneration time and the peak height of Mo-S. We found that the peak height of Mo-S reached a constant value 16 minutes after from the start of regeneration (Fig. 1, right). This suggests that the Mo sulfide on the catalyst had changed to Mo oxide completely, that is, the regeneration was complete at that time. Hence, this time may represent the minimum time required for regeneration.

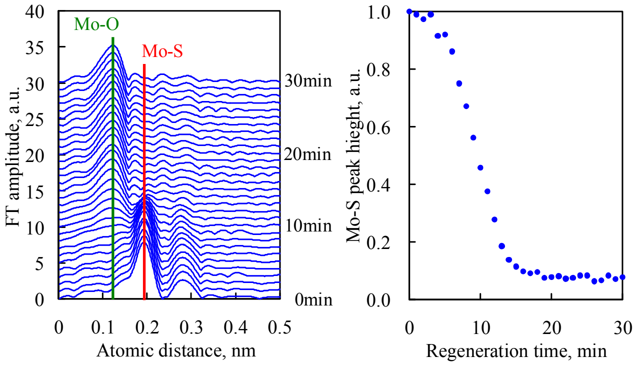

Fig. 1: FT of Mo K-edge EXAFS and regeneration time dependence of Mo-S-peak-height.

We also studied the relationship between the Mo-S peak heights of Mo sulfide in the FTs of the EXAFS spectra obtained from catalysts regenerated at T-100 °C and T+100 °C and the minimum regeneration times. Eventually, we determined the relationship between the relative regeneration temperature and the regeneration time (Fig. 2). We found that the minimum regeneration time for the catalyst regenerated at T-100 °C was about 1.9 times longer than that for the catalyst regenerated at T °C. On the other hand, the minimum time for the catalyst regenerated at T+100 °C was about 0.8 times that for the catalyst regenerated at T °C.

These results suggest that the minimum time required for regeneration increases as the regeneration temperature decreases.

This study was conducted with the cooperation with the Industrial Application Program of the Photon Factory.

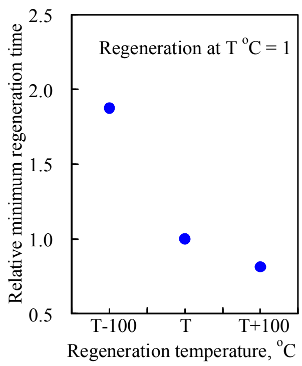

Fig. 2: Regeneration-temperature dependence of regeneration time.

References

[1] A. Nishijima *et al.*, Catalyst Deactivation, 39 (1987).

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