

In-situ EXAFS study on spent CoMo and NiCoMo HDS catalysts 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 spent catalysts is becoming increasingly important. We 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 activities of regenerated CoMo and NiCoMo 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, we 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

In this study, we regenerated aluminum oxide-supported CoMo and NiCoMo spent catalysts which had been used, respectively, in the HDS of gas oil and that of vacuum gas oil in a refinery. 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 several 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 of obtained at the regeneration temperature, T °C, for the CoMo catalyst are shown on the left in Figure 1. The shapes of the FTs of the EXAFS 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, 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 about 17 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.

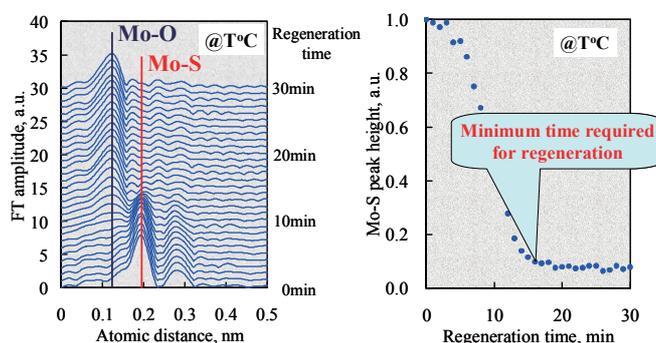


Fig. 1: FT of Mo K-edge EXAFS and regeneration time dependence of Mo-S-peak-height (CoMo catalyst).

We then examined the FTs of the EXAFS obtained from catalysts regenerated at various temperatures, and studied the relationship between the Mo-S peak heights and the minimum regeneration times. Eventually, we determined the relationship between the regeneration temperature and the regeneration time. In Fig. 2, the relationships are shown for both the CoMo and NiCoMo catalyst. We found for both the catalysts that the minimum regeneration times decrease and reach constant values as the regeneration temperature increases. We also found that the minimum regeneration time of the NiCoMo catalyst is longer than that of the CoMo catalyst.

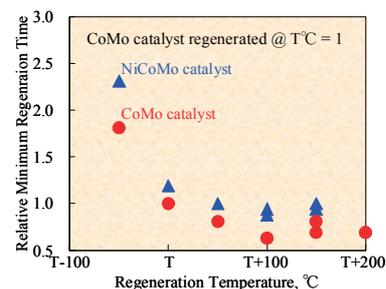


Fig. 2: Regeneration-temperature dependence of regeneration time.

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References

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

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