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In-situ EXAFS study on spent NiCoMo HDS catalyst during regeneration

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Introduction

The hydrodesulfurization (HDS) catalysts used in oil refineries are deactivated through use [1]. However, the spent catalysts can be reused after a regeneration process in which coke deposits 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, such as the temperature, time and air flow rate, with the goal being 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 and the regeneration time. It was thought that the time required for regeneration would vary depending on the air flow rate during regeneration. In this study, we investigated the chemical-state change of the Mo species on a NiCoMo spent catalyst during regeneration by way of *in-situ* Mo K-edge EXAFS measurements, the objective being to optimize the regeneration time and air flow rate.

Experimental

In this study, we regenerated an aluminum oxide-supported NiCoMo spent catalyst which had been used in a refinery. In the regeneration process, Mo sulfides (the active Mo species) on the spent catalyst are converted to Mo oxides through oxidation. The chemical-state changes of the Mo species were observed by way of Mo K-edge in-situ EXAFS measurements in transmission mode on station NW10A of the Photon Factory Advanced Ring (PF-AR). Regeneration was performed by placing the spent catalyst in an in-situ EXAFS cell and heating at the regeneration temperature (T oC) under flowing air atmosphere at different flow rates. The catalyst was kept under a flowing nitrogen atmosphere as it was being heated to the target temperature, T oC. Once the target temperature was reached, the nitrogen gas was changed to air and EXAFS spectra were collected at one-minute intervals.

Results and Discussion

The EXAFS Fourier transforms (FTs) obtained at the regeneration temperature T oC and the air flow rate Vml/min are shown in Figure 1. The shapes of the EXAFS FTs changed over time during regeneration. Thus, we focused our attention on the Mo-S peaks originating from Mo sulfide on the catalyst in the EXAFS FTs. We found that the peak disappeared around 15 minutes after the start of regeneration. This suggests that the Mo sulfide on the catalyst had been completely converted to Mo oxide, that is, the regeneration was complete at that time. Hence, this time may represent the minimum time required for regeneration.

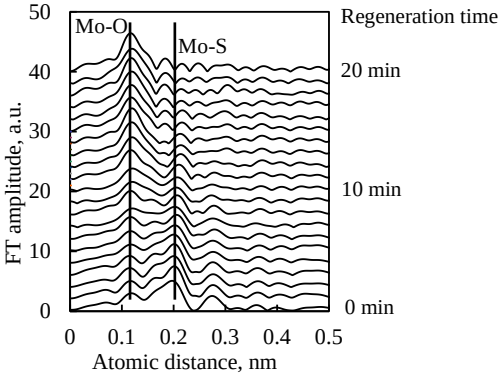

Fig. 1: FTs of Mo K-edge EXAFS of NiCoMo catalyst.

We then examined the EXAFS FTs of catalysts regenerated at various air flow rates. Eventually, we determined the relationship between the air flow rate and the minimum regeneration time at regeneration temperature T oC, as shown in Figure 2, in which the air flow rate Vml/min was defined as 1 and the minimum regeneration time at the air flow rate Vml/min was also defined as 1. We found that the minimum regeneration time decreased almost linearly as the air flow rate increased.

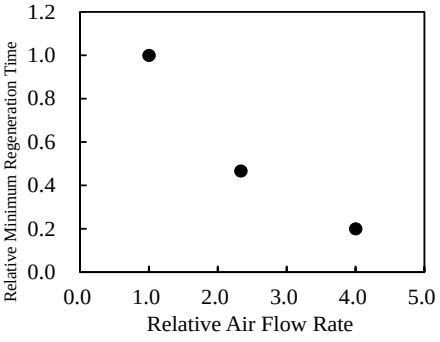

Fig. 2: Air-flow-rate vs. regeneration time.

References

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

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