

## In situ EXAFS study of spent hydrodesulfurization catalyst during regeneration process

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### Introduction

The hydrodesulfurization (HDS) catalyst used in an oil refinery deactivates during the run [1]. The spent catalysts can be reused after the regeneration process. However, the ratio of reusable catalyst is limited since the regeneration condition is not optimized. From the environmental point of view, the role of the catalyst regeneration in refineries becomes more and more important. In order to increase the regenerated catalysts, the regeneration process should be well understood to optimize the regeneration condition.

Here, we report on the chemical-state changes of Mo species in the spent CoMo HDS catalyst during heat treatment corresponding to the regeneration process.

### Experimental

A CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst used for two years in the HDS process of gas oil in a refinery was examined by EXAFS. The Mo K-edge EXAFS measurements in transmission mode were carried out at NW10A. The catalyst was placed in a sample cell where the temperature was controlled under a flowing air environment.

### Result and Discussion

In situ EXAFS measurements were carried out in the following two conditions. In condition 1, EXAFS spectra were collected continuously for about 50 minutes while the spent catalyst was kept heated at 200, 300 and 400 °C under a flowing air atmosphere (10mL/min). In condition 2, the spectra were collected continuously for about 100 minutes while the catalyst was kept heated at 220 °C under a flowing air atmosphere (10, 50 or 100 mL/min).

(1) Condition 1 (Fig.1)

When the spent catalyst was kept heated at 200 °C, the peak intensities of Mo-S and Mo-Mo of MoS<sub>2</sub> in the Fourier transforms of EXAFS decreased slightly as the heating time passed. In contrast, that of Mo-O of MoO<sub>3</sub> increased slightly. This means that MoS<sub>2</sub>, namely the active species on the spent catalyst, was slowly oxidized to MoO<sub>3</sub> at 200°C. When the catalyst was kept heated over 300 °C, the peak intensities of Mo-S and Mo-Mo decreased dramatically as time passed. In contrast, that of Mo-O increased dramatically. This means that MoS<sub>2</sub> was quickly oxidized to MoO<sub>3</sub> over 300 °C.

These results suggested that MoS<sub>2</sub> might be oxidized faster at higher temperatures under certain flowing air conditions.

(2) Condition 2 (Fig.2)

When the spent catalyst was kept heated under a flowing air atmosphere at the rate of 10mL/min, the peak intensities of Mo-S and Mo-Mo of MoS<sub>2</sub> decreased

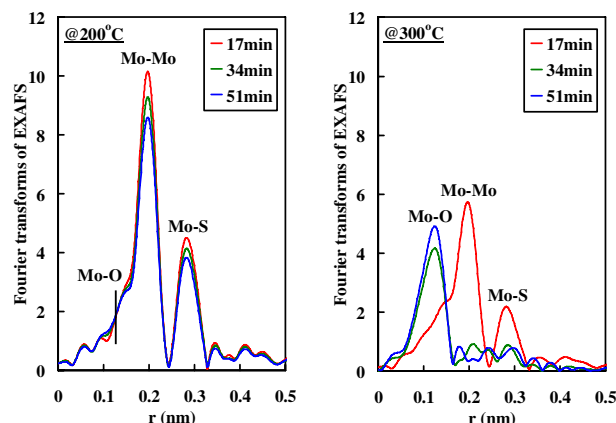


Fig.1 Fourier transforms of EXAFS of catalysts (condition 1)

slightly as time passed. In contrast, that of Mo-O of MoO<sub>3</sub> increased slightly. This means that MoS<sub>2</sub> was slowly oxidized to MoO<sub>3</sub> under a flowing air atmosphere at the rate of 10mL/min. When the catalyst was kept heated under flowing air atmospheres over 50mL/min, the peak intensities of Mo-S and Mo-Mo decreased dramatically as time passed. Meanwhile, that of Mo-O increased dramatically. This means that MoS<sub>2</sub> was quickly oxidized to MoO<sub>3</sub> under flowing air atmospheres at over 50mL/min.

These facts suggested that MoS<sub>2</sub> might be oxidized faster at certain temperatures under flowing air atmospheres at higher rates.

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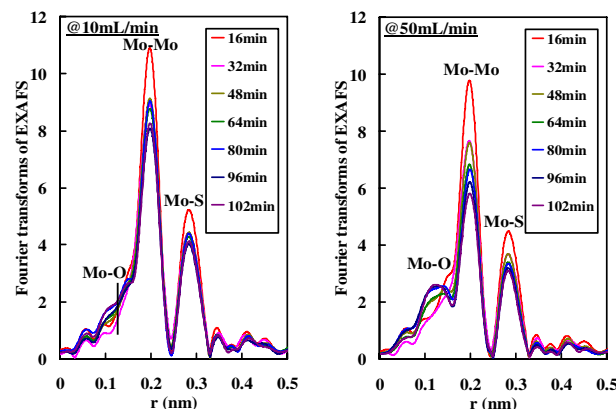


Fig.2 Fourier transforms of EXAFS of catalysts (condition 2)

### References

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

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