

In situ EXAFS study of used hydrodesulfurization catalyst during heat treatment

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Introduction

The catalytic activity of catalysts used in the hydrodesulfurization process in a refinery decreases gradually if used for a long time [1], [2]. The catalysts whose catalytic activity has decreased are, if possible, regenerated and reused in the refinery. If the catalysts cannot be sufficiently regenerated, they are usually disposed of. From an environmental point of view, it becomes more and more important to reduce the volume of disposed catalysts in refineries, so the number of catalysts made reusable by regeneration should be increased. In order to increase the number of reusable catalysts, the optimal regeneration method and condition should be researched. Because one of the factors governing catalytic activity is loaded metals on supports, it is necessary to examine the structure of metals during the regeneration process.

Here, we report on the structural changes of Mo species in the CoMo hydrodesulfurization catalyst during heat treatment corresponding to the regeneration process.

Experimental

The CoMo/Al₂O₃ catalyst examined in this study was used for two years in a refinery for hydrodesulfurization of gas oil. The Mo K-edge EXAFS measurements were carried out at BL-9C. The catalyst was placed in a sample cell where the temperature was controlled under a flowing N₂ gas and/or air environment, and the EXAFS spectra were collected in transmission mode.

Result and Discussion

Experiments were carried out under different heat-treatment conditions. In heat-treatment condition 1, EXAFS spectra were collected at a certain temperature for 30 minutes while the catalyst was heated under flowing gas atmospheres (Fig.1). In heat-treatment condition 2, the spectra were collected every 20 minutes while the temperature was kept at 300°C or 400°C under flowing N₂ (40mL/min) + air (10mL/min) atmospheres.

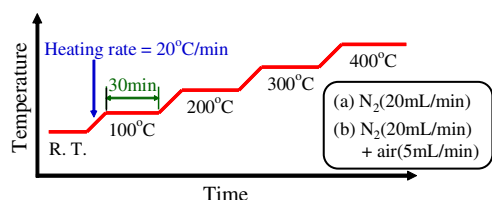


Fig. 1 Heat-treatment condition 1

(Heat-treatment condition 1) As the temperature increased under both N₂ and N₂ + air atmospheres, the intensities of the peaks of Mo-S and Mo-Mo of MoS₂, namely, the sulfided active metal on the CoMo catalyst,

became weaker due to thermal factors (Fig.2). The intensities of these peaks observed at 400°C under N₂ + air atmosphere were apparently weaker than those observed under N₂ atmosphere. This suggested that the structure of MoS₂ might change at 400°C because of the reaction between Mo species and oxygen in the air.

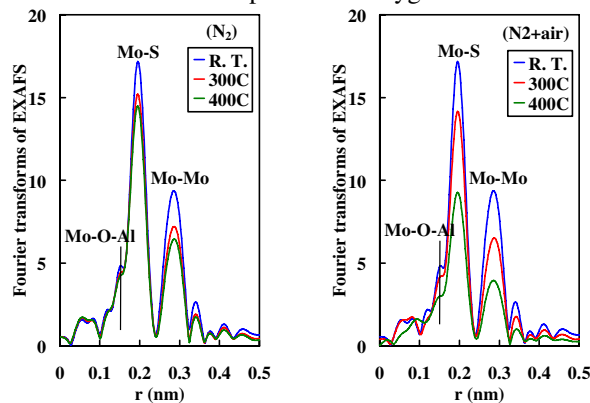


Fig.2 Fourier transforms of EXAFS of catalysts (condition 1)

(Heat-treatment condition 2) As the heat-treatment time passed at both 300°C and 400°C, the intensities of the peaks of Mo-S and Mo-Mo of MoS₂ became weaker (Fig.3). This suggested that the structure of MoS₂ might change and the amount of MoS₂ might decrease as time passed. Further, when the catalyst was heated to 400°C, MoS₂ might be oxidized rapidly because of a high decrease rate of the peak intensity of both Mo-S and Mo-Mo of MoS₂.

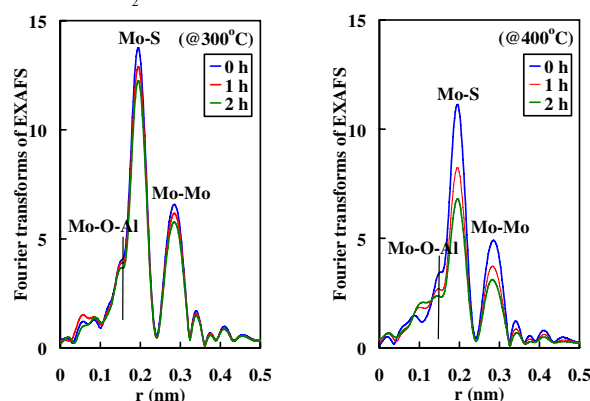


Fig.3 Fourier transforms of EXAFS of catalysts (condition 2)

This study was financially supported by a grant from the Japan Petroleum Energy Center.

References

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