Applied Science

NW10A/2007C008

XAFS study on HDS catalysts regenerated at various temperatures

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Introduction

The hydrodesulfurization (HDS) catalyst used in an oil refinery is deactivated during operation [1]. The spent catalyst can be reused after a regeneration process, whereby cokes deposited on the catalyst are removed. From an environmental point of view, 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.

Here, we report on the relationship between the chemical state and structure of Mo species on a regenerated CoMo HDS catalyst and its catalytic activity.

Experimental

A $CoMo/Al_2O_3$ catalyst used in the HDS processing of gas oil in an oil refinery was regenerated on a laboratory scale. The regeneration was performed by heating the spent catalyst in an electric furnace under a flowing air atmosphere. Cokes deposited on the catalyst burn and Mo sulfides on the catalyst are oxidized to Mo oxides.

The HDS activities of the laboratory-scale regenerated catalysts were estimated using a bench-scale plant. The chemical states and structures of the Mo species on the regenerated catalysts were examined by way of Mo K-edge XAFS measurements in transmission mode at NW10A.

Results and Discussion

The HDS activity of the laboratory-scale regenerated catalysts increased as the regeneration temperature decreased (Fig. 1). To determine why the activity varies depending on the regeneration temperature, we analyzed the Mo species on the catalysts using Mo K-edge XANES and EXAFS. The XANES spectra of the regenerated catalysts showed different patterns depending on the regeneration temperature (Fig. 2). To estimate the ratios of Mo oxides on the catalysts, the spectra of the regenerated catalysts were pattern-fitted with those of fresh and spent catalysts corresponding to Mo oxides and Mo sulfides on the catalysts. The activity of the regenerated catalysts increased as the ratio of Mo oxides decreased, or as the regeneration temperature decreased. Furthermore, the activity increased as the intensity of the Mo-O peak (originating from the Mo oxides) in the FT of EXAFS decreased, or as the regeneration temperature decreased (Fig.3). This indicates that the activity increased as the coordination number of the Mo oxides decreased.

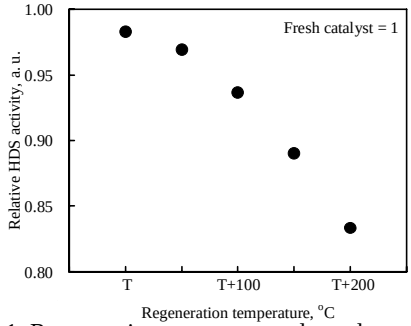

Fig.1 Regeneration-temperature dependence of HDS activity (T: temperature where the maximum HDS activity was observed).

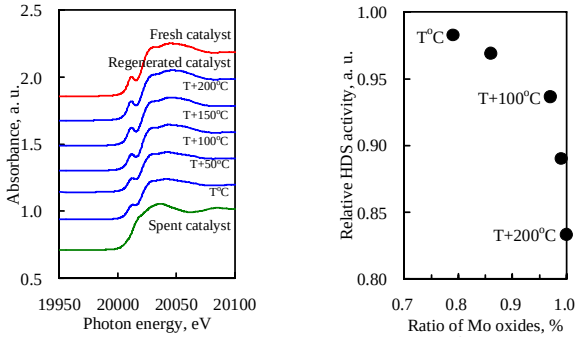

Fig.2 Mo K-edge XANES spectra and ratio-of-Mo-oxides dependence of HDS activity.

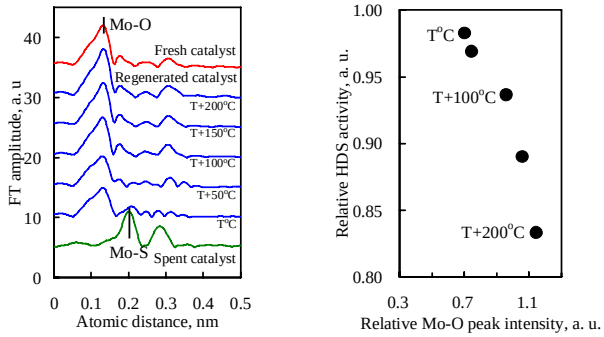

Fig.3 FT of Mo K-edge EXAFS and Mo-O-peak-intensity dependence of HDS activity.

These results suggest that a high recovery of activity can be expected when the spent catalyst is regenerated at a lower temperature where (a) less Mo oxides would be present and (b) the Mo-oxide particles would be smaller.

This study was conducted with financial support from the Japan Petroleum Energy Center.

Reference

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

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