

## Mo K-edge XAFS analysis of CoMo catalyst used in HDS unit using feeds of LGO mixed with components of heavy fuel oil

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### Introduction

When a mixture of light gas oil (LGO) and light cycle oil (LCO), a component of heavy fuel oil, and fed into a hydrodesulfurization (HDS) unit to produce diesel fuel, the catalyst in the HDS unit is deactivated rapidly[1]. In contrast, when the feed is LGO mixed with residue desulfurization gas oil (RDS-GO), another component of heavy fuel oil, the catalyst is deactivated slowly.

In this study, we investigated the chemical states and structures of the loaded metal molybdenum on spent CoMo catalysts from an HDS unit by way of Mo K-edge XAFS measurements in order to understand the mechanism of catalyst deactivation when the HDS feed is LGO mixed with components of heavy fuel oil.

### Experimental

For the Mo K-edge XAFS measurements, we prepared spent aluminum oxide-supported CoMo catalysts which had been used for different times on stream in the HDS unit in a bench scale plant, using feeds of LGOs mixed with 15 vol% of either LCO or RDS-GO.

Before the XAFS measurements, the spent catalysts were subjected to Soxhlet extraction using toluene for 12 hours to remove the oil on them. The XAFS measurements were conducted in transmission mode on station NW10A at the Photon Factory Advanced Ring (PF-AR).

### Results and Discussion

The XANES spectra of the spent catalysts showed slightly different patterns depending on the time on stream (Fig. 1 left). Thus, in order to understand the differences, we estimated the ratios of the active species MoS<sub>2</sub> to the total Mo content, i.e., the degree of sulfurization of the loaded metal Mo on the catalysts. The spectra of the spent catalysts were then pattern-fitted with those of the reference reagents MoS<sub>2</sub> and MoO<sub>3</sub>.

The ratios of the active species MoS<sub>2</sub> on both the catalyst used in the HDS unit using a feed of LGO mixed with LCO (hereafter, LCO mixed feed) and that used in the HDS unit using a feed of LGO mixed with RDS-GO (hereafter, RDS-GO mixed feed) increased with the time on stream (Table 1). There was no great difference in the ratios of the active species MoS<sub>2</sub> on the above-mentioned catalysts at any time on stream.

Furthermore, the heights of the Mo-S peaks (originating from the active species MoS<sub>2</sub>) in the of EXAFS of the catalysts used in the HDS unit using both the LCO mixed feed and RDS-GO mixed feed increased with the time on stream (Fig. 1 right, Table 1). This indicates that the coordination number of the MoS<sub>2</sub>, i.e., the degree of

aggregation of the active species MoS<sub>2</sub> on the catalyst, increased as the time on stream increased. There were no great differences in the coordination numbers of the MoS<sub>2</sub> between the two catalysts at any time on stream.

These results suggest that the deactivation behavior of catalysts used in an HDS unit might not be affected by the chemical state and structure of the active species Mo on the catalysts when using feeds of LGOs mixed with components of heavy fuel oils.

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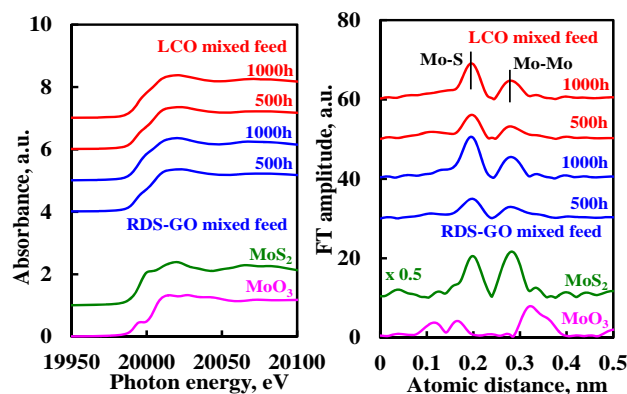


Fig. 1: Mo K-edge XANES spectra (left) and FTs of EXAFS (right) of CoMo spent catalysts.

Table 1 Results of XAFS analysis

Feed	Time on Stream, h	Ratio of MoS <sub>2</sub>	Mo-S Peak height, a. u.
LCO mixed feed	500	0.42	6.1
	1000	0.56	9.1
RDS-GO mixed feed	500	0.40	5.0
	1000	0.64	10.6

### References

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