

## Local structure analysis of metal sulfide catalysts for HDS by means of in situ fluorescence X-ray absorption spectroscopy

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### Introduction

Currently, Co-Mo sulfide catalysts are used for HDS treatment. It is well known that catalytic synergy generates between Co and Mo sulfides in the catalyst system. Numerous studies have been made to clarify the cause of the synergy effects by means of XAFS. But the information about active site of the Co-Mo catalysts is not enough under the reaction condition. The characterization of the catalyst during HDS reaction is necessary to clarify HDS mechanisms and catalyst improvement. In this study, we investigated the local structure analysis of supported Co-Mo sulfide catalysts under the sulfidation and thiophene HDS reaction conditions by means of in situ fluorescence XAFS.

### Experimental

A continuous flow reaction line at atmospheric pressure was constructed in the beamline hatch at BL-9A. An in situ fluorescence XAFS cell was designed to have two windows for collection of incident and fluorescence X-ray. The reaction gas was treated by a post-catalyst, NaOH solution, ZnO column and combustor installed in the reaction line. The concentration of H<sub>2</sub>S at outlet of the line was reduced upto less than 1ppm. The catalyst samples were pressed to self-supported disks. The disk was sulfided in a 5% of H<sub>2</sub>S/H<sub>2</sub> gas (50ml/min) at 623 K. Then a 4% of thiophene/H<sub>2</sub> gas (50ml/min) was flowed to the sample at 623 K. Co K-edge XAFS spectra for Co-Mo catalysts were measured using a Lytle detector with a Fe filter. The synchrotron radiation was monochromatized by a Si(111) monochromator. CoS<sub>x</sub>-MoS<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and CoS<sub>x</sub>-MoS<sub>x</sub>/NaY catalysts were prepared by a CVD method using Mo(CO)<sub>6</sub> and Co(CO)<sub>3</sub>(NO).

### Results and Discussion

Fig.1 shows Co K-edge XANES spectra for CoS<sub>x</sub>-MoS<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> in a flow of H<sub>2</sub>S/H<sub>2</sub> gas at room temperature. The spectrum measured in the air shows a sharp white line due to O<sub>2</sub> adsorption. But the peak intensity was immediately reduced by a flow of H<sub>2</sub>S/H<sub>2</sub>. Fig.2 shows Fourier transforms of k<sup>3</sup>-weighted EXAFS oscillations of Co K-edge for Co-Mo sulfide catalysts measured at 623 K in the H<sub>2</sub>S/H<sub>2</sub> flow, H<sub>2</sub> flow and HDS reaction. The difference in FT peak intensity is not observed between of catalysts measured in the H<sub>2</sub> flow and HDS reaction. It is considered that in the HDS reaction, Co atoms are highly unsaturated.

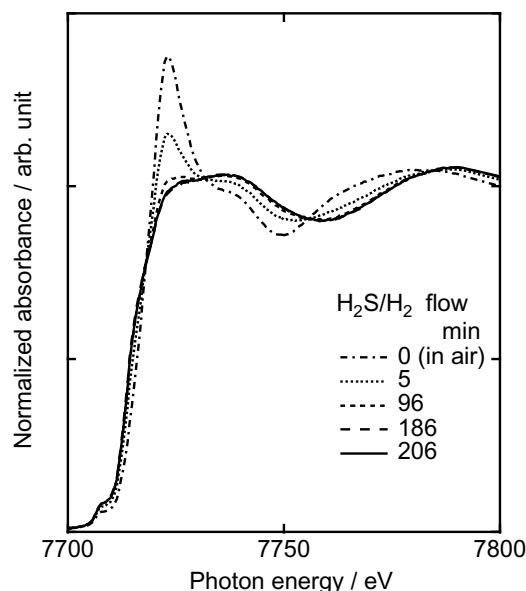


Fig. 1 Co K-edge XANES spectra for Co-Mo sulfide catalysts measured at room temperature in H<sub>2</sub>S/H<sub>2</sub> flow.

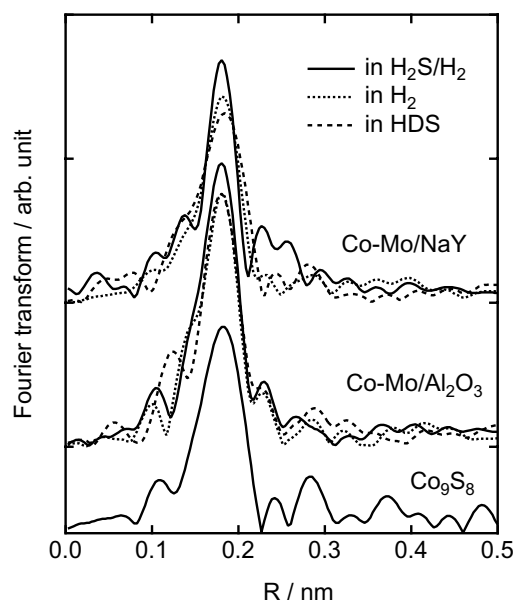


Fig. 2. Fourier transforms of k<sup>3</sup>-weighted EXAFS oscillations of Co K-edge for Co-Mo sulfide catalysts measured at 673 K in the H<sub>2</sub>S/H<sub>2</sub> flow, H<sub>2</sub> flow and HDS reaction.

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