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S K-edge XANES Study on Reaction Films Formed by Automotive Engine Oil

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1 Introduction

The fuel-saving performance of automotive lubricants greatly depends on the composition and structure of the reaction films formed on metal surfaces when additives in the lubricant react with the metal surface.

In this study, we prepared reaction films measuring several tens of nm in thickness on metal surfaces using an automotive engine oil and a friction tester. By varying the test oil temperature, we examined the relationship between the test oil temperature, the friction coefficient that can be taken as a measure of fuel-saving performance, and the chemistry of the obtained film.

2 Experiment

The rolling and sliding friction test was used to prepare reaction films and to measure the friction coefficients for the test automotive engine oil formulated with zinc dialkyl dithiophosphate (ZnDTP), an anti-wear additive, molybdenum dialkyldithiocarbamate (MoDTC), a friction modifier, and calcium sulfonate, a detergent, at four different test oil temperatures. The reaction films formed on the steel discs were then subjected to X-ray absorption near edge structure (XANES) measurements.

The S K-edge XANES measurements in the conversion electron yield mode were carried out on BL-9A at the Photon Factory.

3 Results and Discussion

The relationship between the test oil temperature during the friction test and the friction coefficient was examined. It was found that the reaction films formed at higher test oil temperatures gave lower friction coefficients as shown in Fig. 1.

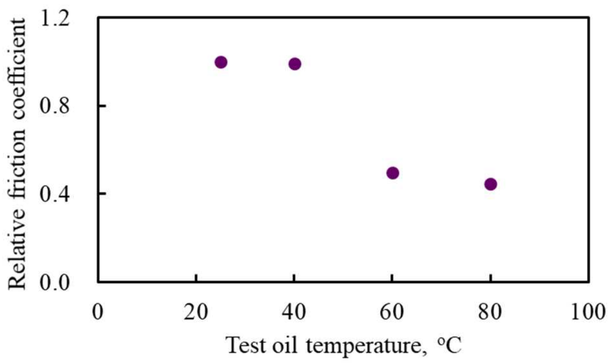

Fig. 1: Test oil temperature dependence of relative friction coefficient.

Sulfur-containing compounds such as ZnDTP and MoDTC in automotive engine oils are thought to react readily with metal surfaces and play an important role in the formation of reaction films. So, to clarify whether the test oil temperature affects the chemistry of sulfur species in the reaction films, the S K-edge XANES spectra were examined. It was found that the shape of the XANES spectra of reaction films changed when the test oil temperature varied (Fig. 2). This indicates that the chemistry of sulfur species in the films changed when the

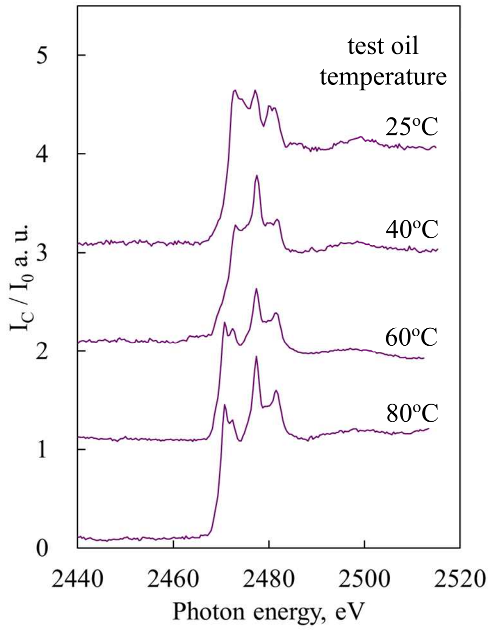

Fig. 2: S K-edge XANES spectra of reaction films formed at various test oil temperatures.

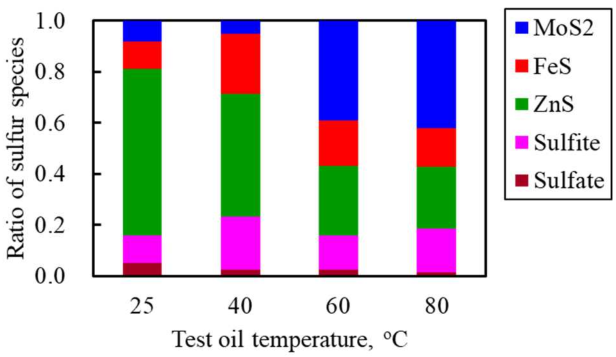

Fig. 3: Ratio of sulfur species in reaction films.

test oil temperature varied. So, to clarify the chemistry of the sulfur species, we estimated the ratios of the sulfur species in the reaction films by pattern-fitting the XANES spectra of the films with the those of sulfur-containing model compounds, such as FeS, MoS_2, ZnS, sulfite, and sulfate, that were expected to be in the reaction films. As a result of pattern-fitting, it was found that the compositions of sulfur species in the reaction films formed at different test oil temperatures were different as shown in Fig. 3. Thus, the test oil temperature during the friction test affects the ratio of sulfur-containing species in the reaction films. Furthermore, we focused on MoS_2, which is thought to reduce the friction coefficient. It was found that the reaction films formed at higher test oil temperatures gave the higher ratios of MoS_2.

The aforementioned results indicate the following: the lowering of friction coefficients of the reaction films formed at higher test oil temperatures is the result of the higher ratios of MoS_2 in the films (Fig. 4).

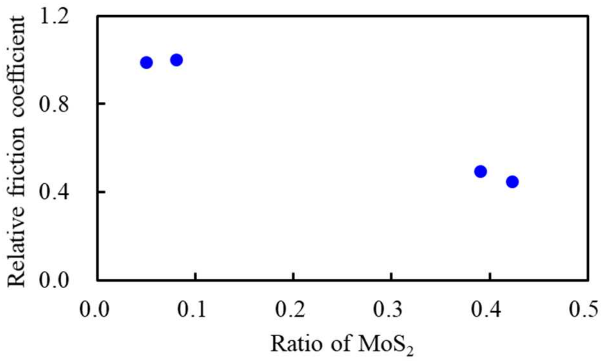

Fig. 4: Ratio of MoS_2 dependence of relative friction coefficient.

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