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XAFS Study on Decomposition of Molybdenum Dialkyl Phosphorodithioate in Commercial Engine Oils

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Abstract. The local structure around Mo atoms in fuel-saving engine oils has been investigated by XAFS using laboratory scale equipment. The EXAFS results suggest that the local structure of the Mo atoms in fresh engine oils is similar to that in the molybdenum dialkyl phosphorodithioate. It is also suggested that the molybdenum compound in the oils changes to a Mo oxide in which a Mo atom is coordinated by six oxygen atoms after 2000km running. XANES spectra of the compounds show that the coordination geometry around the Mo atoms in the Mo oxide is similar to that in MoO_3 rather than MoO_2 . The deterioration of anti-friction effect of the engine oils after use coincides with Mo oxide formation.

1. INTRODUCTION

Cooling, sealing, an anti-corrosion abilities, as well as good lubricating ability, are required for engine oils. Different kinds of additives are usually mixed with engine oils for these purposes. A commercial engine oil including a small quantity of organic molybdenum compound as an anti-friction additive has recently been placed on the market. However, the additive effect on the anti-friction decreased with car running and was lost after 4000km running. Therefore, the information of the structure around Mo atoms in the oils is very important to develop an anti-friction engine oils. In the present study, the local structure around a Mo atom in an engine oil containing an organic molybdenum compound has been investigated by measuring Mo-K absorption spectra.

2. EXPERIMENTAL

2.1 Samples

Different kinds of commercial engine oils containing a small quantity of organic molybdenum compound (about 0.02wt.% of Mo) were used for car running and subjected to XAFS measurements. The lubrication ability of the engine oils after car running was estimated using a crossed-pin type lubricant tester. The results of the lubrication tests for the engine oils with and without a Mo compound and the engine oils used for XAFS measurements are shown in Figure 1.

The Mo-K XAFS of the engine oils before and after the car running were measured. Mo metal foil (35 μm thick), Mo-DTP additive (containing about 9wt.% of Mo), and extra pure MoO_2 , MoO_3 , and MoS_2 were used as reference materials in this study.

2.2 Measurement

XAFS spectra in the vicinity of the Mo-K absorption edge were measured in transmission mode. An X-ray generator with a Cu rotating anode was operated at 40kV-180mA. Continuous X-ray from the target was monochromatized by a Ge(220) Johansson type bent crystal. The intensities of the incident X-ray beam (I_0) transmitted beam (I) were measured by an ionization chamber and a solid state detector, respectively. A sample holder with an X-ray pass length of 60mm was used to measure the X-ray absorption spectrum of a small quantity of Mo in the engine oil. The energy region to measure the spectra was divided into three parts; the low energy side of the edge (19.4-19.8keV), the high energy side (20.7-21.0keV), and near the absorption edge (19.8-20.7keV), and the stepping width of each energy region was set at 30eV, 6eV, and 2.5eV, respectively. The X-ray intensity at each different data point was measured using the fixed time method.

3. RESULTS AND DISCUSSION

3.1 EXAFS

Curve fitting analysis was performed to obtain structural parameters. The curve fitting results are shown in Table 1, suggesting the following points for the Mo compound after car running.

- ① The second and third peaks corresponding to Mo-S and Mo-Mo pairs, respectively, disappeared with an increase in the car running distance, and the position of the first peak corresponding to the Mo-O pair changed with car running.
- ② The bonds between the Mo atom and the coordinated oxygen atoms in oils A and B after 4000km car running are ascribed to Mo-O or Mo-OH and Mo=O, respectively, because their interatomic distances of 2.06 and 1.65Å, respectively, are close to the values for single and double bonds for a Mo-O pair. In all cases, it was found that the structure of the Mo compound added to the engine oil as an anti-friction additive was dissociated by the car running about 2000km, and that the liberated Mo atom subsequently combines with six oxygen atoms. It seems that most of the Mo coordinated by six oxygen atoms is dispersed at random in the oil because a peak due to the Mo-Mo pair is not observed in the Fourier transforms.

3.2 XANES

The derivative XANES spectra are shown in Figures 2 and 3. These derivative spectra showed the following:

- ①The two kinds of engine oils, A and B, are similar to each other in the initial state.
- ②The curves after car running are also similar to each other, and to that of MoO₃ in which the Mo atom is surrounded by six oxygen atoms.

Although a Mo atom in crystalline MoO₃ differs from that of a Mo atom in crystalline MoO₂, the inter-atomic distances between the Mo atom and oxygen atoms in the crystalline MoO₂ have an anisotropic distribution in a range from 1.84 to 2.34Å. While, those of MoO₃ have a relatively isotropic distribution in a range of from 1.94 to 2.07Å. From the crystallographic knowledge, we can say that the geometrical local structure around the Mo atom in the engine oil after the car running is similar to that in crystalline MoO₃ compared to that in crystalline MoO₂. These XANES results are also supported by the results of the EXAFS analysis.

4. CONCLUSION

The Mo-K absorption measurements were carried out using laboratory scale XAFS equipment to analyze the deterioration mechanism of the commercial engine oils containing a small quantity of organic molybdenum compound. The results obtained are summarized as follows:

- (1)The local structure around a Mo atom in the engine oils at the initial state is basically similar to that of the Mo-DTP additive.
- (2)The local structure around Mo in the engine oils is changed after car running. The liberated Mo atom produced by the dissociation is coordinated by six oxygen atoms. The oxygen coordination of the Mo atom is similar to that in the crystalline MoO₃.
- (3)The structural change of the Mo compound is related to the friction coefficient. Therefore, the deterioration in the anti-friction effect of the engine oils after car running coincides with Mo oxide formation.
- (4)It is found that even a small quantity of elements may be measured by XAFS. The laboratory scale XAFS equipment was verified to be useful in determining the local structure of dilute system.

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Figure 1 : Change of the friction coefficient during car running. [○:oil (A), ●:oil (B), △:Mo free oil]

Table 1 : Curve fitting results

Sample	Bond	r (Å)	N	λ (Å)	σ (Å)	
A	Mo-DTP additive	Mo-O	1.67 _s	1.5	1.8	0.05
		Mo-S	2.24 _s	3.9	2.0	0.06
		Mo-Mo	2.78 _s	1.2	6.0	0.08
	-1 (0km)	Mo-O	1.97 _s	3.6	3.9	0.05
		Mo-S	2.69 _s	3.2	4.2	0.04
		Mo-Mo	3.05 _s	2.0	12	0.06
	-2 (1000km)	Mo-O	2.01 _s	5.8	4.2	0.03
		Mo-O	2.06 _s	6.3	6.0	0.04
		-3 (4000km)	Mo-O	1.96 _s	3.9	3.0
Mo-S	2.68 _s		3.2	2.3	0.08	
B	-1 (0km)		Mo-Mo	3.05 _s	2.0	12
		Mo-O	1.81 _s	2.7	4.1	0.09
		Mo-S	1.80 _s	3.5	4.2	0.09
	-2 (1000km)	Mo-O	1.80 _s	3.5	4.2	0.09
		Mo-S	1.80 _s	3.5	4.2	0.09
		Mo-O	1.65 _s	6.2	3.0	0.12
	-3 (4000km)	Mo-O	1.65 _s	6.2	3.0	0.12
		Mo-S	2.68 _s	3.2	2.3	0.08
		Mo-Mo	3.05 _s	2.0	12	0.10

Figure 2 : Derivative curves for the references. [a:Mo, b:MoO₂, c:MoO₃, d:MoS₂, e:Mo-DTP additive]

Figure 3 : Derivative curves for the engine oils. [A-1, -2 and -3:oil (A), B-1, -2 and -3:oil (B)]