P and S K-edge XANES measurements of tribofilms formed on steel disks in conversion electron yield and fluorescence yield modes

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Introduction
The fuel efficiency of vehicles will continue to be an important issue, due to the needs to conserve natural resources and protect the global environment. One of the ways to improve fuel efficiency is to control the lubricating properties of oils used in the lubricated parts of vehicles. Additive formulations in oils are important to control the lubricating properties. For example, formulations to reduce the friction coefficients of engine oils and to enhance the friction coefficients of transmission oils are needed. Therefore, we have studied tribofilm chemistry in order to understand the effects of additive formulations on the lubricating properties of both engine and transmission oils.

In this report, we summarize the results of P and S K-edge XANES measurements of tribofilms formed on steel disks.

Experimental
Tribofilms were formed on steel disks with the oils formulated for different friction coefficients as described Table 1, using a friction testing machine. The disks were cleaned with n-hexane prior to the XANES measurements.

P and S K-edge XANES measurements were carried out in conversion electron yield (CEY) and fluorescence yield (FY) modes, using a Lytle detector at BL-9A.

Table 1: XANES-measured tribofilms

<table>
<thead>
<tr>
<th>Triofilm</th>
<th>Oil</th>
<th>Friction coefficient</th>
<th>XANES mode</th>
<th>CEY</th>
<th>FY</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-H-μ</td>
<td>Engine oil</td>
<td>High</td>
<td>×</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>E-M-μ</td>
<td>Engine oil</td>
<td>Middle</td>
<td>×</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>E-L-μ</td>
<td>Engine oil</td>
<td>Low</td>
<td>○</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>T-H-μ</td>
<td>Transmission oil</td>
<td>High</td>
<td>○</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>T-L-μ</td>
<td>Transmission oil</td>
<td>Low</td>
<td>○</td>
<td>○</td>
<td>○</td>
</tr>
</tbody>
</table>

1) ○: measured, ×: unmeasured

Results and Discussion

Tribofilms formed by engine oils
Figure 1 shows the S K-edge XANES spectra of tribofilms formed by three different engine oils measured in the FY mode (bulk analysis). It is obvious from the figure that the spectra are significantly different. This suggests that the sulfur composition in the bulk of tribofilms may be different depending on the additive formulation of the engine oils.

In contrast, all the P K-edge XANES spectra (not shown) of the tribofilms measured in the FY mode are almost identical, suggesting that the phosphorous composition in the bulk of tribofilms may be similar.

Tribofilms formed by transmission oils
Figure 2 shows the S K-edge XANES spectra of tribofilms formed by two different transmission oils, measured in both the FY (bulk analysis) and CEY mode (surface analysis). In the figure, the spectra are different, suggesting that the sulfur composition in the tribofilms may be different, depending on the additive formulation of the transmission oils. Furthermore, the spectra of both the T-H-μ and T-L-μ tribofilms measured in the FY and CEY modes are different. This suggests that the sulfur compositions in the bulk and surface of the tribofilms may be different, and that surface modifications may take place in the tribofilms.

In contrast, all the P K-edge XANES spectra (not shown) of the tribofilms measured in both the FY and CEY modes are almost identical, suggesting that the phosphorous composition in the bulk and surface of tribofilms may be similar.

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