XAFS study on supported ruthenium catalysts for lignin gasification in supercritical water

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Introduction
Gasification of lignin, which is a major fraction of woody biomass, is needed for its efficient use as a high quality energy source. Supercritical gasification is a useful technique because of elimination of drying process of biomass [1]. We discovered that charcoal-supported ruthenium salt catalysts were active as a charcoal-supported ruthenium metal catalyst and the activity depended on the kinds of ruthenium salts used [2]. In this paper, we report the structure of ruthenium species for charcoal-supported ruthenium salt catalysts by a XAFS analysis.

Experimental
The catalysts used were prepared by an impregnation method using activated charcoal powder and an aqueous solution of ruthenium (III) chloride (RuCl3/C) or ruthenium (III) nitrosyl nitrate solution in dilute nitric acid (Ru(NO)(NO3)3/C) [2]. Also, a commercially available charcoal-supported ruthenium catalyst (Ru/C) was used. Gasification of lignin was carried out in a SUS316 tube. The catalyst, lignin, and water were loaded in the tube and gas in the reactor was purged with argon gas. The reactor was submerged into a molten-salt bath at 673 K for 1 h. After the reaction, the tube was submerged into a water bath for cooling to ambient temperature. The catalyst samples were recovered from the SUS reactors quickly and filled into XAFS cells as water suspensions. XAFS measurements were performed using a synchrotron radiation ring at AR-NW10A with a Si(311) double-crystal monochromator in transmission mode. The EXAFS spectra were analyzed by the UWXAFS package.

Results and discussion
Table 1 shows gasification rates in supercritical water (water density 0.5 g cm−3) over the ruthenium-based catalysts for 1 h at 673 K. The Ru(NO)(NO3)3/C and RuCl3/C catalysts, which were not reduced during the preparation, showed lignin gasification activities. The Ru(NO)(NO3)3/C was almost as active as Ru/C for the gasification; however, the RuCl3/C catalyst was three times less active than those catalysts. Figure 1 shows Fourier transforms of k3-weighted Ru K-edge EXAFS spectra for the ruthenium catalysts after the lignin gasification. The peaks of Ru-Ru were observed at 0.23 nm (phase shift uncorrected) in RuCl3/C and Ru(NO)(NO3)3/C after the lignin gasification, indicating that ruthenium metal particles were formed in both ruthenium salt supported catalysts during the lignin gasification. The curve-fitting analysis showed that the coordination number (CN) of Ru-Ru metal bond for Ru(NO)(NO3)3/C and Ru/C were 6.1±1.2 and 6.7±1.1, respectively, indicating that small ruthenium metal clusters with number of atoms between 12 and 40 [3]. On the other hand, the CN of RuCl3/C was 11.2±2.3, confirming that large ruthenium metal particles were formed in RuCl3/C. XAFS would explain that Ru(NO)(NO3)3/C showed high gasification activity because small active ruthenium metal particles were formed on the charcoal support.

Table 1: Initial rate and composition of lignin gasification in supercritical water.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Gasification rate (10−6 mol cat-g−1 s−1)</th>
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<tbody>
<tr>
<td>Ru/C</td>
<td>15.4</td>
</tr>
<tr>
<td>RuCl3/C</td>
<td>5.6</td>
</tr>
<tr>
<td>Ru(NO)(NO3)3/C</td>
<td>14.2</td>
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Figure 1. Fourier transforms of k3-weighted Ru K-edge EXAFS spectra.

References
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