

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 need 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. The XAFS spectra of the catalysts, which were exposed to air, were measured at ambient temperature. 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 *k*³-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.

Catalyst	Gasification rate (10 ⁶ mol cat ⁻¹ g ⁻¹ s ⁻¹)
Ru/C	15.4
RuCl ₃ /C	5.6
Ru(NO)(NO ₃) ₃ /C	14.2

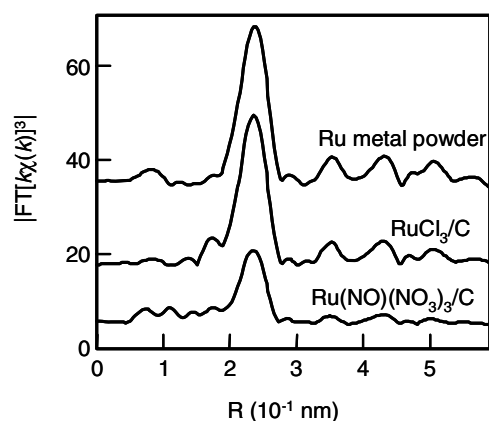


Figure 1. Fourier transforms of *k*³-weighted Ru K-edge EXAFS spectra.

References

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