

XAFS study on structural change of supported ruthenium catalysts during lignin gasification in supercritical water

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Introduction

Biomass and organic wastes have attracted much attention as renewable energy source because the green house effect of carbon dioxide from the combustion of fossil fuel has to be reduced in view of an environmental problem of global warming. The gasification of lignin, which is a major fraction of woody biomass, is needed for its efficient use as a high quality energy source. Supercritical water ($T_c = 647.3$ K, $P_c = 22.1$ MPa) gasification are efficient because of elimination of drying the biomass; therefore, supercritical water gasification is a promising technique to reduce the lignin gasification temperature.

We investigated the effects of the supports, ruthenium precursors, and counter anions of ruthenium salts on the lignin gasification over ruthenium trivalent salts supported on activated charcoal carbon and titanium oxide.

Experimental

We prepared RuCl_3/C , $\text{Ru}(\text{NO})(\text{NO}_3)_3/\text{C}$, $\text{RuCl}_3/\text{TiO}_2$, and $\text{Ru}(\text{NO})(\text{NO}_3)_3/\text{TiO}_2$, based on the corresponding ruthenium precursors and supports by an impregnation method.[1-3] Gasification of lignin was carried out in a SUS 316 tube, of which inner volume was 6.0 cm^3 . The catalyst (0.15 g), lignin (0.10 g), and water (3.0 g) were loaded in the tube and the reactor was purged with argon gas. The reactor was submerged into a molten-salt bath at 673 K for a given reaction time. XAFS measurements were performed using a synchrotron radiation ring at AR-NW10A, Photon Factory, KEK with a Si (311) double-crystal monochromator in transmission mode. The EXAFS spectra were analyzed by the UWXAFS package. After background subtraction, a k^3 -weighted EXAFS function in the k range of $30\text{--}140 \text{ nm}^{-1}$ was Fourier transformed into an R-space.

Results and discussion

The activities of lignin gasification were influenced significantly by the precursor of ruthenium species. The gas yields over supported ruthenium (III) nitrosyl nitrate catalysts ($\text{Ru}(\text{NO})(\text{NO}_3)_3/\text{C}$ and $\text{Ru}(\text{NO})(\text{NO}_3)_3/\text{TiO}_2$) showed about three times higher activities than those over supported ruthenium (III) chloride catalysts (RuCl_3/C and $\text{RuCl}_3/\text{TiO}_2$). The XANES spectra of the $\text{RuCl}_3/\text{TiO}_2$, $\text{Ru}(\text{NO})(\text{NO}_3)_3/\text{TiO}_2$, RuCl_3/C , and $\text{Ru}(\text{NO})(\text{NO}_3)_3/\text{C}$

catalysts before the lignin gasification were similar to those of the corresponding precursors, ruthenium (III) chloride and ruthenium (III) nitrosyl nitrate. The XANES spectra of those catalysts after the lignin gasification were similar to XANES of the ruthenium metal, indicating that ruthenium species of these catalysts were reduced to ruthenium metal during the lignin gasification. Figure 4 shows Fourier transforms of k^3 -weighted EXAFS spectra at Ru K-edge of the $\text{RuCl}_3/\text{TiO}_2$, $\text{Ru}(\text{NO})(\text{NO}_3)_3/\text{TiO}_2$, RuCl_3/C , and $\text{Ru}(\text{NO})(\text{NO}_3)_3/\text{C}$ catalysts after the lignin gasification in supercritical water at 673 K. The ruthenium metal particle sizes as well as the lignin gasification activities were influenced significantly by the precursor of ruthenium species.

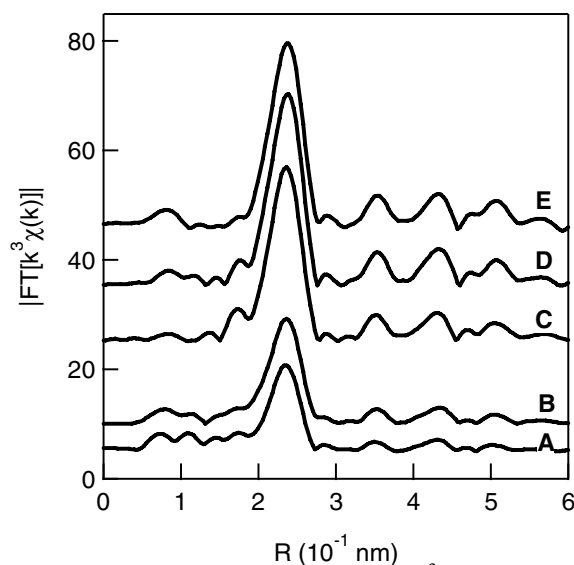


Figure 1. Fourier transforms of k^3 -weighted EXAFS spectra at Ru K-edge for supported ruthenium trivalent-salt catalysts after the lignin gasification in supercritical water at 673 K for 1 h. (A) $\text{Ru}(\text{NO})(\text{NO}_3)_3/\text{C}$, (B) $\text{Ru}(\text{NO})(\text{NO}_3)_3/\text{TiO}_2$, (C) RuCl_3/C , (D) $\text{RuCl}_3/\text{TiO}_2$, and (E) Ru metal foil.

References

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