

Structural Study of Supported Ruthenium Catalysts for Biomass Transformation to Fuel Gas in Supercritical Water

Lignin is a major fraction of woody biomass (10–30 wt%), and its gasification to fuel is needed for efficient use of the biomass. Supported ruthenium salts show catalytic activities for lignin gasification in supercritical water at 673 K. Ruthenium (III) nitrosyl nitrate on charcoal ($\text{Ru}(\text{NO})(\text{NO}_3)_3/\text{C}$) showed higher activity for gasification than ruthenium (III) chloride on charcoal (RuCl_3/C). An EXAFS analysis revealed that ruthenium metal particles were formed in both catalysts during gasification, and the particles formed in $\text{Ru}(\text{NO})(\text{NO}_3)_3/\text{C}$ were smaller than those formed in RuCl_3/C . We conclude that well-dispersed, small ruthenium metal particles are active for the lignin gasification in supercritical water.

The utilization of lignin, a major fraction of woody biomass, has attracted much attention as a renewable energy source because the green house effect of carbon dioxide released from the combustion of fossil fuel must be reduced in order to control global warming. The gasification of lignin to methane and hydrogen is needed for its efficient use as a high quality energy source in a fuel cell or as a liquid fuel using the Fisher-Tropsch reaction. Supercritical water ($T_c = 647.3 \text{ K}$, $P_c = 22.1 \text{ MPa}$) gasification is a promising technique for reducing the lignin gasification temperature from 1073 K to 673 K [1–4]. In this paper, we report the catalytic performance and active structure of charcoal-supported ruthenium (III) salts for lignin gasification in supercritical water at 673 K.

Figure 1 shows the gas yields from lignin gasification in supercritical water as a function of reaction time. Lignin in the reactor was almost completely gasified over the $\text{Ru}(\text{NO})(\text{NO}_3)_3/\text{C}$ catalyst in supercritical water at 673 K in 3 h; however, lignin gasification over the

RuCl_3/C catalyst reached a plateau at about 30 C% lignin conversion after 1 h. The percentage of hydrogen in the gaseous products over $\text{Ru}(\text{NO})(\text{NO}_3)_3/\text{C}$ was ca. 10% at 20 min and decreased to ca. 3% after 1 h. In contrast, the percentage of methane over the $\text{Ru}(\text{NO})(\text{NO}_3)_3/\text{C}$ catalyst increased with an increase in reaction time from 20 min to 1 h, indicating that methanation proceeded during the gasification. The hydrogen and carbon dioxide composition of the gaseous products over the RuCl_3/C catalyst was higher and the percentage of methane was lower, indicating that the RuCl_3/C catalyst is inactive for methanation.

EXAFS spectra at the Ru K-edge for the RuCl_3/C and $\text{Ru}(\text{NO})(\text{NO}_3)_3/\text{C}$ catalysts recorded after lignin gasification in supercritical water for 1 h at 673 K were also studied. Figure 2 shows the EXAFS oscillations and Fourier transforms of the k^3 -weighted EXAFS spectra [5–7]. Peaks corresponding to Ru–Ru were observed at 0.23 nm (phase shift uncorrected) in RuCl_3/C

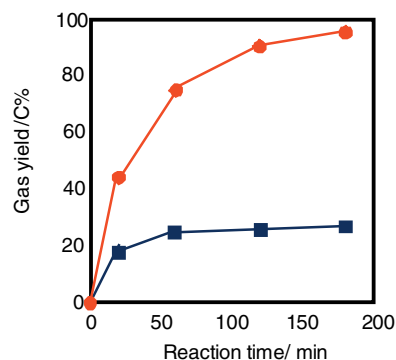


Figure 1
Carbon yield of gaseous product for lignin gasification in supercritical water at 673 K (RuCl_3/C (■), $\text{Ru}(\text{NO})(\text{NO}_3)_3/\text{C}$ (●)).

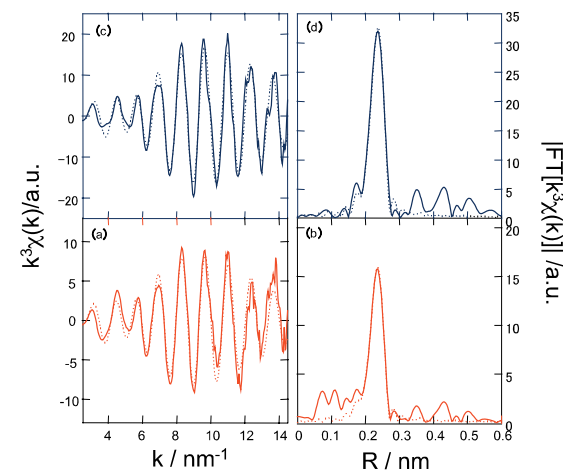


Figure 2
EXAFS oscillations $k^3\chi(k)$ (a, c) and their Fourier transforms (b, d) for RuCl_3/C (a, b), $\text{Ru}(\text{NO})(\text{NO}_3)_3/\text{C}$ (c, d) after lignin gasification in supercritical water at 673 K for 1 h. Solid and dotted lines represent the experimental and the fitted results, respectively.

and $\text{Ru}(\text{NO})(\text{NO}_3)_3/\text{C}$, indicating that ruthenium metal particles were formed in both of the catalysts during the lignin gasification. The Ru–Ru bond distance for the RuCl_3/C and $\text{Ru}(\text{NO})(\text{NO}_3)_3/\text{C}$ catalysts corresponds with that of ruthenium metal, indicating metal particle formation in both samples. The coordination number of the Ru–Ru bond for RuCl_3/C is 11.2 ± 2.3 , confirming that large ruthenium metal particles were formed in RuCl_3/C . On the other hand, the coordination number of $\text{Ru}(\text{NO})(\text{NO}_3)_3/\text{C}$ is 6.1 ± 1.2 , which corresponds to ruthenium metal clusters of between 12 and 40 atoms. The above results lead to the conclusion that the size of ruthenium metal particles formed by the reduction of ruthenium trivalent salts during the lignin gasification in supercritical water depends on ruthenium precursors and dramatically affects gasification activity. Lignin gasification occurs via two steps; (i) lignin decomposes to alkylphenols and formaldehyde via hydrolysis in supercritical water without a catalyst, and (ii) the gasification of alkylphenols and formaldehyde in the presence of supported ruthenium catalysts [2]. The latter step was catalyzed by ruthenium metal even for un-reduced catalysts RuCl_3/C and $\text{Ru}(\text{NO})(\text{NO}_3)_3/\text{C}$.

We observed that the ruthenium (III) species in the supported ruthenium salts were reduced to ruthenium metal particles, which were responsible for the lignin gasification activities in supercritical water.

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