

Characterization of the Rh/CeO₂/SiO₂ Catalyst for Partial oxidation of Tar from Biomass

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Introduction

One of the promising methods of energy utilization of biomass is gasification to hydrogen and synthesis gas. Biomass has been gasified at high temperature in the conventional process. Recently, our group has reported that Rh/CeO₂/SiO₂ was very effective to the gasification of biomass [1]. The performance of tar removal and the stability of Rh/CeO₂/SiO₂ were also much higher than conventional methods, such as steam reforming Ni catalyst, dolomite and or non-catalyst. We suggest that these high performances of Rh/CeO₂/SiO₂ are mainly due to combination of high activity of reforming and combustion caused by the synergetic effect between Rh and CeO₂. The results of temperature-programmed reduction and oxidation support this suggestion. And in this research, we have carried out the characterization of Rh/CeO₂/SiO₂ in order to confirm the interaction between Rh and CeO₂.

Experimental

The Rh/CeO₂/SiO₂ catalyst was prepared by incipient wetness method using acetone solution of Rh(C₅H₇O₂)₃ (Soekawa) and CeO₂/SiO₂ support. The loading amount of Rh was 1.2 mass%. After evaporating the acetone solvent, the catalyst was dried at 383 K for 12 h.

The catalyst was crushed and pressed to the disk (0.5 mm, 10 mm ϕ) for EXAFS measurements. Oxide sample was pretreated at 873 K under 30 cc/min O₂ flow for 0.5 h. Reduced sample was pretreated at 873 K under H₂ flow for 0.5 h following the same treatment of Oxide sample. After treatment, the sample disk was transformed to the measurement cell without exposing to air. Rh *K*-edge EXAFS spectra were measured by transmission mode at 77 K. After back ground subtraction, *k*³ weighted EXAFS functions were Fourier transformed into *R* space and the two or three-shell fitting were analyzed by curve fitting.

Results and Discussion

Fig. 1 shows the *k*³-weighted Rh *K*-edge EXAFS oscillations for oxidized(a) and reduced(b) Rh/CeO₂/SiO₂. From the fitting results of EXAFS data of reduced catalyst, we could fit the spectrum only Rh-Rh species and coordination number of Rh-Rh was around 12. And the spectrum was very similar to that of Rh foil. This result shows that almost all Rh exist as metal particles in reduced Rh/CeO₂/SiO₂. And from the results of hydrogen adsorption measurement, the size of the particles of Rh metal was assumed about 7 nm. On the other hand, in the case of oxidized Rh/CeO₂/SiO₂, we have use three-shell fitting to fit the spectrum by coordinated with longer Rh-

Rh species (Rh₂O₃ lattice), Rh-O (Rh₂O₃ lattice), and Rh-Ce shells. And this Rh-Ce shell exhibits the interaction between Rh and Ce. In addition, from the coordination number of Rh-O and Rh-Rh, it is suggest that Rh was oxidized and dispersed as two or three layers of Rh and O atoms on the CeO₂ support. From the results of temperature-programmed reduction and oxidation measurement, it was shown that the existence of Rh species on CeO₂ support enhanced the reducibility of CeO₂. And it can be corresponds to the higher reforming activity of Rh/CeO₂/SiO₂. The result of EXAFS analysis supports theses synergy between Rh and Ce.

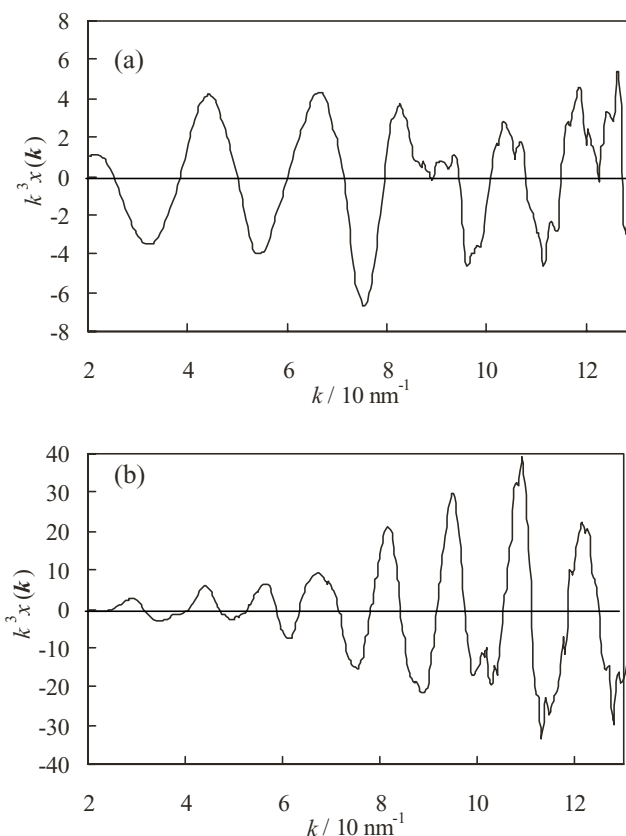


Fig. 1. *k*³-weighted Rh *K*-edge EXAFS for Rh/CeO₂/SiO₂ (a) Oxidized (b) Reduced

References

- [1] K. Tomishige, et al. *Appl. Catal. A: Gen.* **246** (2003) 103.
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