

Structural Study of Charcoal Supported Noble Metal Salt Catalysts for Gasification of Organosolv-lignin in Supercritical Water

Aritomo Yamaguchi, Norihito Hiyoshi, Osamu Sato, and Masayuki Shirai*

Research Center for Compact Chemical System, National Institute of Advanced Industrial Science and Technology (AIST), Sendai 983-8551, Japan

1 Introduction

Biomass and organic wastes have attracted much attention as renewable energy sources because the green house effect of carbon dioxide from the combustion of fossil fuel has to be reduced. Lignin is a major fraction of woody biomass and the gasification of lignin to hydrogen and methane is needed for its efficient use. We have reported that charcoal-supported ruthenium (III) salts were reduced to form highly-dispersed ruthenium metal particles during the lignin gasification, which were active for the lignin gasification [1]. We investigated the catalytic activity for the lignin gasification of various charcoal supported metal salt catalysts and investigated the structural change for metal species by X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analyses [2].

2 Experiment

The various catalysts used in this work were prepared by an impregnation method using activated charcoal powder and solutions of metal salts. Gasification of lignin was carried out in a batch reactor [1,2].

XANES and EXAFS measurements were performed using a synchrotron radiation ring in transmission mode at AR-NW10A, PF-KEK. The EXAFS spectra were analyzed by the UWXAFS package. The backscattering amplitudes and phase shifts were calculated by the FEFF8 code.

3 Results and Discussion

Fig. 1 shows XANES spectra for supported rhodium salt catalysts before and after lignin gasification in supercritical water at 673 K. The XANES spectra of the RhCl_3/C , $\text{Rh}(\text{NO}_3)_3/\text{C}$, and $\text{Rh}(\text{acac})_3/\text{C}$ (Fig. 1 (a)) before the lignin gasification changed drastically after the gasification (Fig. 1 (b)) and the XANES spectra after the gasification were the same as the rhodium metal. These results indicate that rhodium salt species were reduced to metal states during the lignin gasification. The same phenomena were observed in ruthenium, platinum, and palladium catalysts. EXAFS analysis also showed that small metal particles were formed on the charcoal support after the gasification for the supported metal salt catalysts without chloride anion and showed higher activities for the lignin gasification. Lower activities and deactivation of supported metal chloride catalysts were caused by the smaller number of metal sites and surface poisoning by chloride anions.

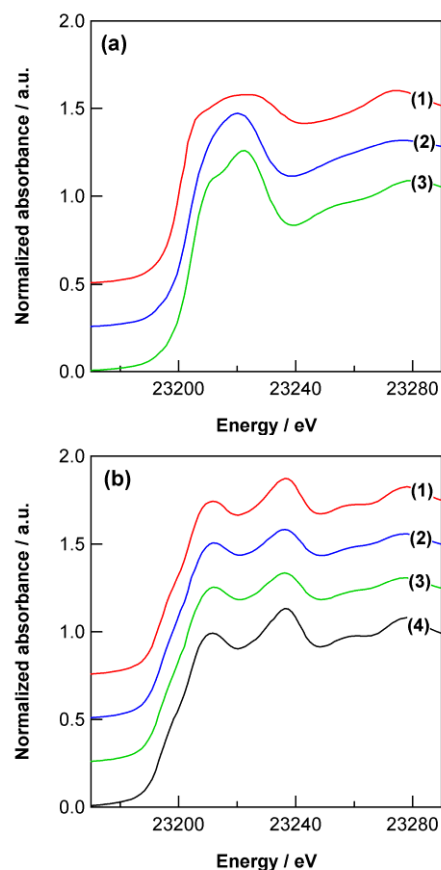


Fig. 1: XANES spectra for supported metal salt catalysts before and after lignin gasification in supercritical water at 673 K. (a) Rh K-edge: (1) RhCl_3/C , (2) $\text{Rh}(\text{NO}_3)_3/\text{C}$, and (3) $\text{Rh}(\text{acac})_3/\text{C}$ before the gasification, and (b) (1) RhCl_3/C , (2) $\text{Rh}(\text{NO}_3)_3/\text{C}$, and (3) $\text{Rh}(\text{acac})_3/\text{C}$ after the gasification (1 h), and (4) rhodium metal foil.

References

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* m.shirai@aist.go.jp