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XAFS Study of Charcoal-Supported Palladium and Nickel Bimetal Catalysts for Lignin Gasification in Supercritical Water

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1 Introduction

Lignin is a major fraction of woody biomass and a polymer having aromatic compounds as monomer units. The gasification of lignin to hydrogen and methane 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 of lignin is a promising technique because of a decrease of lignin gasification temperature. 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 applied palladium and nickel salts to the lignin gasification in order to prepare highly-dispersed Pd-Ni alloy particles on charcoal support during the lignin gasification and to investigate activity of Pd-Ni alloy, compared with the individual monometals [2].

2 Experiment

The catalysts used in this work were prepared by an impregnation method using activated charcoal powder and aqueous solutions of tetraamminepalladiuum (II) nitrate or nickel (II) nitrate. The supported binary metal salt catalysts (denoted as Pd(II)-Ni(II)/C) were prepared by physically mixing two kinds of supported monometal salt catalysts (denoted as Pd(II)/C and Ni(II)/C).

Gasification of lignin was carried out in a batch reactor. A product yield (C%) was calculated based on the carbon amount of reactant lignin [1,2].

X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (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

The gas yields from the lignin gasification over the Pd(II)-Ni(II)/C catalysts were higher than the linear combination of gas yields over the individual monometals (Fig. 1), indicating that the Pd(II)-Ni(II)/C binary salts catalysts showed the synergetic effect of Pd-Ni. The main peaks in Fourier transforms of k^3-weighted EXAFS for Pd(II)-Ni(II)/C(3:1), Pd(II)-Ni(II)/C(1:1), and Pd(II)-Ni(II)/C(1:3) gradually decrease and shift to the shorter distance with the decrease of Pd/Ni ratio (Fig. 2), indicating the formation of Pd-Ni bond in addition to Pd-Pd bond. EXAFS and XRD analysis show the formation of small Pd-Ni alloy particles, which are the active sites for the lignin gasification.

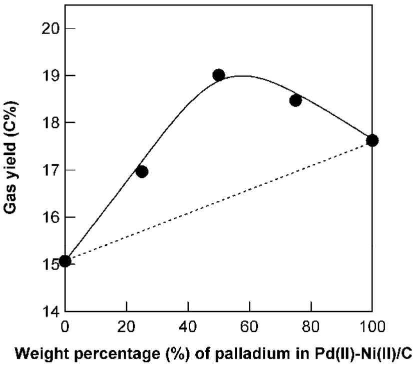

Fig. 1: Gas yield of lignin gasification in supercritical water at 673 K for 1 h over Ni(II)/C, Pd(II)-Ni(II)/C, and Pd(II)/C catalysts.

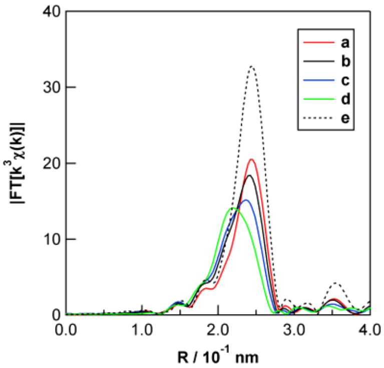

Fig. 2: Fourier transforms of k^3-weighted Pd K-edge EXAFS spectra of Pd(II)-Ni(II)/C and Pd(II)/C catalysts after lignin gasification in supercritical water at 673 K for 1 h (phase shift uncorrected). (a) Pd(II)/C, (b) Pd(II)-Ni(II)/C(3:1), (c) Pd(II)-Ni(II)/C(1:1), (d) Pd(II)-Ni(II)/C(1:3), and (e) reference Pd metal foil.

References

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