Characterization of Pt-Ni bimetallic catalyst for oxidative steam reforming of methane

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Introduction
Oxidative steam reforming of methane is one of the attractive methods for the synthesis gas production for GTL (Gas to Liquid) process because the oxidative reforming is more energy efficient than conventional steam reforming of methane. Recently, our group has found that the addition of trace amount of Pt to Ni catalyst (Pt/Ni=0.01) suppressed the hot spot formation with high activity during the oxidative steam reforming of methane. The Pt-Ni bimetallic particle structure can be influenced according to the preparation method. In this study, we characterized the Pt-Ni bimetallic catalysts using EXAFS.

Experimental
Supported monometallic Ni and Pt catalysts were prepared using the impregnation method. After removal of the solvent, calcined at 773 K in air for 3 h. Pt–Ni bimetallic catalyst was prepared using two methods. One is the sequential (two-step) impregnation method. The calcined monometallic nickel catalyst was reduced at 1123 K for 0.5 h under H2 flow, and then this treated sample was impregnated with the acetone solution of Pt(C5H7O2)2. After removal of the acetone solvent, the catalyst was dried and calcined in air at 573 K for 3 h. The resultant catalyst is denoted as Pt/Ni. The other method is co-impregnation. The precursor is a mixed aqueous solution of Ni(NO3)2·6H2O+H2PtCl6. After co-impregnation, the preparation procedure is identical to that of monometallic catalyst. This resultant catalyst is denoted as Pt+Ni. The number in parentheses refers to the weight percent of the catalyst's metallic component.

The catalysts were treated by H2 at 1123 K for 0.5 h and the samples were pressed into self-supporting 7 mm-diameter wafers under atmosphere, followed by the treatment, again with H2, at 773 K for 0.5 h in the cell. Passivated samples were also prepared as follows: after the catalyst powder was reduced with H2 at 1123 K, it was passivated with 0.5 % O2 in He at room temperature. Then, the passivated catalysts were pressed into disks. Pt L3-edge EXAFS spectra were measured by transmission mode at room temperature. After back ground subtraction, k3 weighted EXAFS functions were Fourier transformed into R space and the one or two-shell fitting were analyzed by curve fitting.

Results and Discussion
Figure 1 shows Fourier transform of Pt L3-edge EXAFS oscillations of various catalysts after H2 reduction and passivation. To compare the resistance to oxidation, we measured EXAFS spectra of the catalysts after passivation. The FT of Pt foil is also shown as a reference. For all catalysts, a peak between 0.15 and 0.30 nm was observed in the FT; they are assignable to the Pt–Pt bond. Table 1 lists their curve fitting results. In cases of Pt–Ni bimetallic catalyst, the contribution of the Pt–Ni bond was detected in curve fitting analysis. These results suggest the formation of Pt–Ni alloy phase by which Pt atoms can partly substitute Ni atoms in Ni metal phase. The coordination numbers of the Pt–Pt bond and Pt–Ni bond over Pt+Ni decreased by passivation pretreatment, which is explainable by the oxidation of metal and this is supported by the increase of the contribution of the Pt–O bond.

Reference