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Surface modification of Ni catalysts with trace Pd
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. In this study, we attempt to use other noble metal, such as Pd. As a characterization, we carried out extended X-ray absorption fine structure (EXAFS).

Experimental

Supported monometallic Ni and Pd catalysts were prepared using the impregnation method After removal of the solvent, calcined at 773 K in air for 3 h. Pd–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 H_2 flow, and then this treated sample was impregnated with the acetone solution of $Pd(C_5H_7O_2)_2$. 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 Pd/Ni. The other method is co-impregnation. The precursor is a mixed aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O + PdCl_2$. After co-impregnation, the preparation procedure is identical to that of monometallic catalyst. This resultant catalyst is denoted as Pd+Ni. The number in parentheses refers to the weight percent of the catalyst's metallic component.

The catalysts were treated by H_2 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 H_2 at 773 K for 0.5 h in the cell. Passivated samples were also prepared as follows: after the catalyst powder was reduced with H_2 at 1123 K, it was passivated with 0.5 % O_2 in He at room temperature. Then, after the passivated catalysts were pressed into disks. Ni *K*-edge EXAFS spectra were measured by transmission mode at room temperature. After back ground subtraction, k^3 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 Ni *K*-edge EXAFS oscillations of various catalysts after H_2 reduction and passivation. To compare the resistance to oxidation, we measured EXAFS spectra of the catalysts after passivation. The FT of Ni 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 Ni–Ni bond. Table 1 lists their curve fitting results. In cases of Pd–Ni bimetallic catalyst, the contribution of the Ni–Pd bond was not detected in curve fitting analysis, which is ascribed to the low molar ratio of noble metal to Ni in these bimetallic catalysts. The coordination number of the Ni–Ni bond on Pd/Ni was a little larger than that on co-impregnation catalyst. The coordination number of the Ni–Ni bond over Ni and Pd+Ni decreased by passivation pretreatment, which is explainable by the oxidation of Ni metal and this is supported by the increase of the contribution of the Ni–O bond.
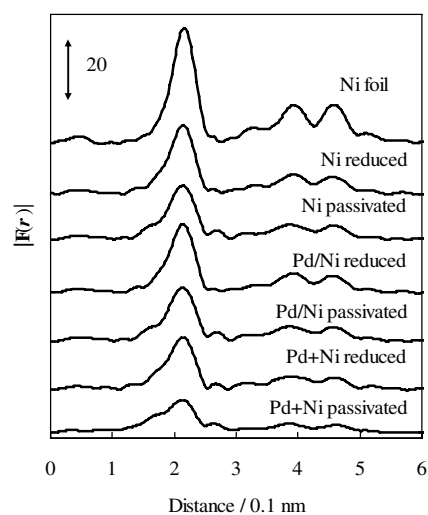

Fig.1 Results of Fourier transform of k^3-weighted Ni *K*-edge EXAFS oscillation of Ni, Pd+Ni and Pd/Ni after the H_2 reduction and passivation. The results of Ni foil is also shown as a reference.

Table 1 Curve fitting of Ni *K*-edge EXAFS of various catalysts

Catalyst	Pretreatment	Shells	*CN*	*R* / 10^{-1} nm
Ni foil		Ni-Ni	12	2.49
Ni(0.9)	reduction	Ni-Ni	9.3±0.2	2.49±0.001
	passivation	Ni-Ni	7.7±0.4	2.49±0.003
		Ni-O	1.6±2.5	2.05±0.034
Pd(0.1)+Ni(0.9)	reduction	Ni-Ni	9.2±0.2	2.48±0.002
	passivation	Ni-Ni	5.3±0.4	2.49±0.004
		Ni-O	3.9±1.4	2.02±0.018
Pd(0.1)/Ni(0.9)	reduction	Ni-Ni	10.5±0.2	2.49±0.001
	passivation	Ni-Ni	9.7±0.4	2.49±0.003
		Ni-O	0.7±1.1	2.04±0.036

Reference

[1]K Tomishige et al. *Appl. Catal. A: Gen.* **318** (2007) 254.

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