

## 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 H<sub>2</sub> flow, and then this treated sample was impregnated with the acetone solution of Pt(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub>. 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(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O+H<sub>2</sub>PtCl<sub>6</sub>. 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 H<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> at 1123 K, it was passivated with 0.5 % O<sub>2</sub> in He at room temperature. Then, after the passivated catalysts were pressed into disks. Pt L<sub>3</sub>-edge EXAFS spectra were measured by transmission mode at room temperature. After background subtraction, k<sup>3</sup> 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 L<sub>3</sub>-edge EXAFS oscillations of various catalysts after H<sub>2</sub> 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 Pd+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.

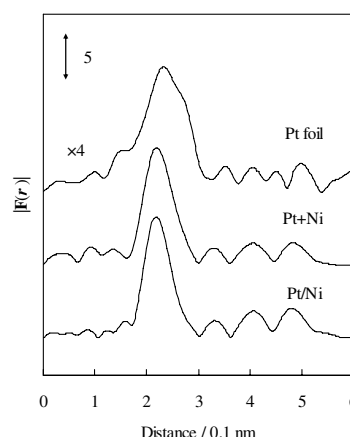


Fig.1 Results of Fourier transform of k<sup>3</sup>-weighted Pt L<sub>3</sub>-edge EXAFS oscillation of Pt+Ni and Pt/Ni after the H<sub>2</sub> reduction. The result of Pt foil is also shown as a reference.

Table 1 Curve fitting of Pt L<sub>3</sub>-edge EXAFS of various catalysts

Catalyst	Pretreatment	Shells	CN	R / 10 <sup>-1</sup> nm
Pt (0.2)	reduction	Pt-Pt	10.5±2.2	2.72±0.02
	passivation	Pt-Pt	10.5±2.3	2.71±0.02
Pt(0.2)+Ni(0.9)	reduction	Pt-Pt	3.7±1.1	2.65±0.01
		Pt-Ni	4.5±0.6	2.52±0.01
	passivation	Pt-Pt	3.2±1.5	2.65±0.02
		Pt-Ni	3.3±0.5	2.51±0.01
Pt(0.2)/Ni(0.9)	reduction	Pt-Pt	2.8±1.0	2.65±0.02
		Pt-Ni	4.3±0.3	2.52±0.01
	passivation	Pt-Pt	2.7±1.1	2.69±0.03
		Pt-Ni	4.2±1.1	2.52±0.02
Pt foil		Pt-Pt	12	2.77

### Reference

[1]K Tomishige et al. *Chem. Eng. Sci.*, in press.

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