

## EXAFS analysis for structure of active site for partial oxidation of methane

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### Introduction

One of the promising technologies of the synthesis gas production is catalytic partial oxidation (CPO) of methane. A lot of catalysts have been developed for the CPO of methane, and typical catalysts as reported previously were the supported Rh catalysts. Recently, our group has found that the addition of Co to Rh/MgO catalyst (Co/Rh=1) promoted the catalytic performance and suppressed the hot spot formation during of CPO of methane<sup>1</sup>. In this research, we carried out the comparative study of Rh/MgO modified with Fe, with Co and with Ni, and the present study focuses on the catalyst structure by extended X-ray absorption fine structure (EXAFS)<sup>2</sup>.

### Experimental

Monometallic Rh/MgO catalysts was prepared using the impregnation method After removal of the solvent, calcined at 773 K in air for 3 h. The bimetallic Rh-M/MgO (M = Fe, Co or Ni) catalyst was prepared using co-impregnation method. The loading amount of Rh was 1.0 wt%, and the additive amounts of M (M = Fe, Co or Ni) were denoted as M/Rh (molar ratio).

Each catalyst powder (150 mg for Fe, Co and Ni K-edge) was treated using H<sub>2</sub> at 1123 K for 0.5 h in a fixed-bed reactor. Each sample was pressed into a self-supporting 7-mm-diameter disk under atmosphere, followed by treatment with H<sub>2</sub> at 773 K for 0.5 h in a cell. After this pretreatment, the sample disk was transferred to the measurement cell using a glove box filled with nitrogen to prevent exposure of the sample disk to air.

### Results and Discussion

In order to evaluate the interaction between Rh and additive base metals, the reduced catalysts were characterized by EXAFS analysis. Figure 1 shows Fourier transform of M (M=Fe(a), Co (b), Ni(c)) K-edge EXAFS oscillations of various catalysts after H<sub>2</sub> reduction, and the curve fitting results of bimetallic catalysts are shown in Table 1. The FT of metal foil and oxide compounds are also shown as a reference. In the case of Rh-Fe/MgO (Fig. 1(a)), the contribution of Fe-O and Fe-Mg bonds was not observed, and this is due to the high reduction degree of Fe on Rh-Fe/MgO. On Rh-Fe/MgO, the good fitting was obtained by two waves of Fe-Fe and Fe-Rh bonds. This is probably because the interaction between Fe and Rh makes the Fe species with fcc structure. In the case of Rh-Co/MgO (Fig. 1(b)), the Co-Rh bond as well

as Co-O, Co-Mg, Co-Co bonds can be assigned. The CN of the Co-Co bond increased gradually with increasing Co amount and the bond distance is almost the same as that in Co metal. One possible explanation of this Co-Co bond is that Co metal particles can be partially formed without the interaction with Rh-Co alloy particles. The CN of the Ni-O and Ni-Mg bonds on Rh-Ni/MgO (Fig. 1(c)) is larger than that of Co-O and Co-Mg bonds on Rh-Co/MgO. This tendency agreed well with the reduction degree of Ni being lower than that of Co.

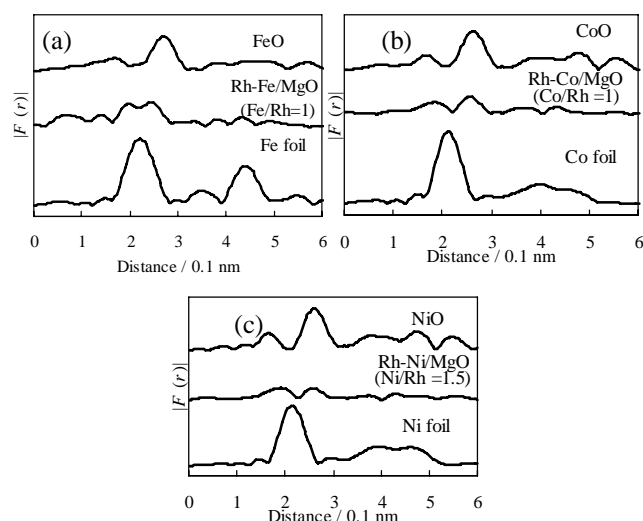


Fig. 1 Results of Fourier transform of  $k^3$ -weighted M (M=Fe, Co, Ni) K-edge EXAFS oscillation of the catalysts after the H<sub>2</sub> reduction.

Table 1 Curve fitting of M K-edge EXAFS of various bimetallic catalysts

Catalyst	Shells	CN	$R / 10^{-1} \text{ nm}$
Rh-Fe/MgO (Fe/Rh=1)	Fe-Fe	7.9±4.1	2.49±0.05
	Fe-Rh	3.6±1.2	2.59±0.01
Rh-Co/MgO (Co/Rh=1)	Co-O	2.8±1.0	2.13±0.03
	Co-Co	2.4±0.8	2.57±0.03
	Co-Rh	2.4±0.5	2.62±0.01
	Co-Mg	4.7±2.2	3.00±0.02
Rh-Ni/MgO (Ni/Rh=1.5)	Ni-O	4.1±1.2	2.10±0.02
	Ni-Ni	1.6±0.9	2.54±0.02
	Ni-Rh	1.9±0.7	2.55±0.01
	Ni-Mg	8.2±1.7	2.97±0.01

### References

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- [2] H. Tanaka et al. *Appl. Catal. A: Gen.* **378** (2010) 175.

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