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

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## Introduction

Partial oxidation of methane is one of the attractive methods for the synthesis gas production for GTL (Gas to Liquid) process because high methane conversion and syngas yield were obtained at short and millisecond contact times in the reaction. We found that the addition of Co to 0.3 wt% Rh/MgO in a suitable amount enhanced $CH_4$ conversion and selectivity for syngas formation, which were beyond those of 1.0 wt% Rh/MgO in the partial oxidation of methane at short contact time. At the same time, results show that Rh/MgO modified with an optimum amount of Co was very effective for suppression of hot spot formation. In this study, we carried out extended X-ray absorption fine structure (EXAFS) as a characterization.

## Experimental

Rh/MgO catalysts were prepared by impregnating MgO with an aqueous solution of $RhCl_3•3H_2O$. The MgO was obtained by calcining $MgCO_3$ at 1423 K for 3 h; the BET surface area of the MgO was determined to be 6.5 $m^2$/g. After impregnation, the solvent was evaporated at 353 K and the sample was dried at 383 K for 12 h and then calcined at 773 K for 3 h. Loading amounts of Rh were 0.3 wt%. Also, Rh/MgO modified with Co was also prepared. Co was added by the co-impregnation method using the mixed aqueous solution of $RhCl_3•3H_2O$ and corresponding nitrate. After co-impregnation, the solvent was evaporated at 353 K and the sample was dried at 383 K for 12 h and then calcined at 773 K for 3 h. Catalysts are denoted as Rh–Co/MgO, and the amount of the additives is described by the molar ratio to Rh as in Rh–Co/MgO (Co/Rh = 1). The loading amount of Rh on Rh–Co/MgO was 0.3 wt%.

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. Rh $K$-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 Rh $K$-edge EXAFS results of catalysts after $H_2$ reduction; curve fitting results are presented in Table 1. On the Rh–Co/MgO catalysts, Rh–Co bonds as well as the Rh–Rh bonds were required for obtaining a good curve fitting result. The coordination number (CN) of the Rh–Co bond increased and the CN of the Rh–Rh bond decreased with increasing Co amount. The bond distance of the Rh–Co bond is 0.257–0.263 nm, which is located between Rh–Rh bond (0.268 nm) in Rh metal and Co–Co bond (0.251 nm) in Co metal. At the same time, the Rh-Rh bond distance on the Rh–Co/MgO catalysts is 0.262–0.264 nm, which is shorter than that in Rh metal (0.268 nm). The curve fitting results suggest alloy formation of Rh and Co, and this results can explain high performance of Rh–Co/MgO (Co/Rh = 1). The catalytic performance of Rh-Co/MgO can be dependent on the surface composition of the Rh-Co alloy particles.

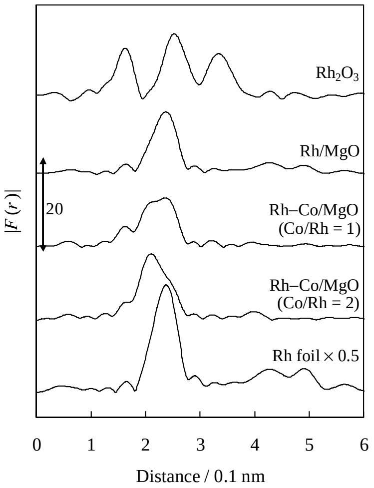

Fig.1 Results of Fourier transform of $k^3$-weighted Rh $K$-edge EXAFS oscillation of catalysts after the $H_2$ reduction. The results of Rh foil and $Rh_2O_3$ are also shown as a reference.

Table 1 Curve fitting results of Rh $K$-edge EXAFS of reduced catalysts.

| Catalyst | Shells | $CN$ | $R$ / $10^{-1}$ nm |
|---|---|---|---|
| $Rh_2O_3$ | Rh-O | 6 | 2.06 |
| Rh/MgO | Rh–Rh | 10.6±0.1 | 2.68±0.01 |
| Rh-Co/MgO | Rh–Rh | 7.4±0.2 | 2.64±0.01 |
| (Co/Rh=1) | Rh–Co | 3.2±0.2 | 2.63±0.02 |
| Rh-Co/MgO | Rh–Rh | 5.7±0.1 | 2.62±0.01 |
| (Co/Rh=2) | Rh–Co | 4.8±0.1 | 2.57±0.01 |
| Rh foil | Rh-Rh | 12 | 2.68 |

## Reference

[1] K Tomishige et al. *J. Catal* ***259*** (2008) 138.

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