

# XAFS Characterization of Ceria-doped Ni/SBA-16 Catalysts for Dry Reforming of Methane

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## Introduction

Improvement of resistance to coking on Ni catalysts is a key issue in dry reforming of methane (DRM). We have prepared Ni-ceria catalysts (Ni/Ce = 1/1) in the cage-like pores of SBA-16 for DRM and investigated the oxidation states and local coordination structures of supported NiCe/SBA-16 catalysts before and after DRM reactions at 973 K by Ce L<sub>III</sub>-edge and Ni K-edge XAFS<sup>[1]</sup>.

## Experimental

NiCe/SBA-16 (5 wt% Ni with molar ratio of Ni/Ce = 1/1) was prepared by an impregnation method, and DRM was conducted at 973 K with CH<sub>4</sub>/CO<sub>2</sub>/H<sub>2</sub> = 1/1/1. Ni K-edge (fluorescent mode) and Ce L<sub>III</sub>-edge (transmission mode) XAFS spectra were measured at 298 K at the BL-9C station of KEK-PF with monochromatized X-rays by Si(111) double crystals. Ni K-edge XANES, EXAFS, and Ce L<sub>III</sub>-edge XANES spectra were analyzed with Iffeffit (Athena and Artemis) ver. 1.2.11. Background subtraction was performed with Autobk and Spline smoothing algorithm in the Athena program. *k*<sup>3</sup>-Weighted Ni K-edge EXAFS oscillations (*k* = 30–130 nm<sup>-1</sup>) were Fourier transformed into *R*-space, and EXAFS curve-fitting analysis was carried out in *R*-space. Fitting parameters were coordination number (CN), interatomic distance (*R*), Debye-Waller factor ( $\sigma^2$ ), and correction-of-edge energy ( $\bullet E_0$ ). Phase shifts and backscattering amplitudes were calculated from the crystal structures of Ni foil and NiO by using the FEFF8 code, and  $S_0^2$  values were determined by their curve-fitting analysis.<sup>[2]</sup>

## Results and Discussion

Valence states of Ce in NiCe/SBA-16 were examined by Ce L<sub>III</sub>-edge XANES as shown in Fig. 1A. Two XANES peaks at 5731.1 and 5738.0 eV were observed at Ce L<sub>III</sub>-edge of CeO<sub>2</sub> with Ce<sup>4+</sup>, whereas a single peak at 5726.6 eV was observed for CeCl<sub>3</sub>·7H<sub>2</sub>O with Ce<sup>3+</sup>. Fresh NiCe/SBA-16 exhibited a typical characteristic of Ce<sup>3+</sup> with a sharp peak at 5726.5 eV, indicating that Ce<sup>3+</sup> was the dominant species in the fresh NiCe/SBA-16 catalyst and stable under the DRM reaction conditions.

Valence states and the local coordination structure of the supported Ni species were examined by Ni K-edge XANES (Fig. 1B) and curve-fitting analysis of Ni K-edge EXAFS. Ni K-edge XANES of fresh NiCe/SBA-16 showed a similar structure to that of Ni foil, and the contribution of Ni-Ni bonds was observed at 0.248 ±

0.001 nm (CN = 10.0 ± 0.9), indicating that metallic Ni was dominant species. Ni K-edge XANES and EXAFS of NiCe/SBA-16 after DRM and those exposed to CH<sub>4</sub> suggested that the metallic Ni species was retained, whose bond distances were 0.249 ± 0.001 nm (CN = 10.4 ± 1.3) and 0.248 ± 0.001 nm (CN = 10.8 ± 0.5), respectively. On the other hand, the exposure of NiCe/SBA-16 to CO<sub>2</sub> led to the partial oxidation of Ni, with contributions of Ni-Ni bonds at 0.248 ± 0.001 nm (CN = 4.6 ± 1.4) attributed to Ni metal, Ni-O bonds at 0.210 ± 0.003 nm (CN = 4.6 ± 1.5) and Ni-Ni bonds at 0.296 ± 0.001 nm (CN = 7.2 ± 1.3) assigned as NiO. The XAFS analysis suggested that under the steady-state DRM conditions in the presence of CH<sub>4</sub>, Ni existed as metallic particles, which would be the active species for DRM.

## References

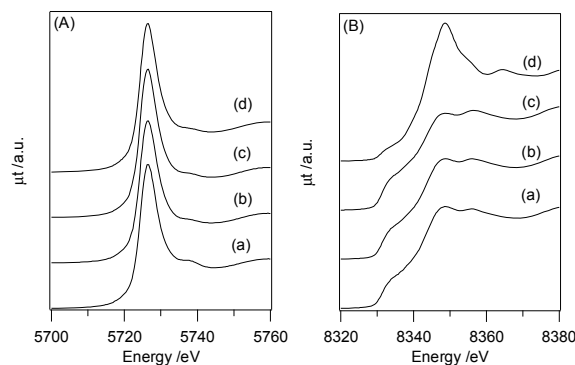


Figure 1 (A) Ce L<sub>III</sub>-edge and (B) Ni K-edge XANES spectra of (a) fresh NiCe/SBA-16, (b) used NiCe/SBA-16 after DRM at 973 K for 100 h, (c) CH<sub>4</sub>-treated NiCe/SBA-16 in 20% CH<sub>4</sub>/He for 2 h at 973 K and (d) CO<sub>2</sub>-treated NiCe/SBA-16 in 20% CO<sub>2</sub>/He for 2 h at 973 K.<sup>[1]</sup>

[1] S. Zhang, S. Muratsugu, N. Ishiguro, M. Tada, submitted.

[2] Y. Chen, J. Shen, N. -X. Chen, *Solid State Commun.*, **2009**, *149*, 121-125; R. W. Cairns, E. Ott, *J. Am. Chem. Soc.* **1933**, *55*, 527-533.

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