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XAFS Characterization of Ni/NaCeTi$_2$O$_6$ Catalysts for CH$_4$ Steam Reforming

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Introduction

Enhancing the reducibility and basicity of support is one of the most promising methods to improve the resistance to coking on Ni catalysts for steam reforming of methane (SRM)[1]. We have succeeded in preparing Ni catalysts loaded on perovskite NaCeTi$_2$O$_6$ (NCT) oxide, which contains both reducible Ce^{3+} and basic Na$^+$ sites, and have investigated the oxidation states and local coordination structures of supported Ni/NCT catalysts before and after SRM reaction at 973 K[2].

Experimental

4 wt% Ni/NCT catalysts were prepared by a wet impregnation method, and SRM reactions were conducted at 973 K with a low H$_2$O/CH$_4$ ratio (1/1). Ni K-edge (fluorescence mode) and Ce L$_{III}$-edge XAFS (transmission mode) spectra were measured at 298 K at the BL-9C and BL-12C stations of KEK-PF with the monochromatized X-rays by Si(111) double crystals. XAFS data were analysed with IFEFFIT (Athena and Arthemis) ver. 1.2.11. Background subtraction was performed with Autobk and Spline smoothing algorithm in the Athena program. k^3-Weighted Ni K-edge EXAFS oscillations (k = 30-130 nm^{-1}) 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 (σ^2), and correction-of-edge energy (ΔE_0). Phase shifts and backscattering amplitudes were calculated from the crystal structure of Ni foil and NiO by using the FEFF8 code, and S_0^2 values were determined by the curve-fitting analysis of Ni foil and NiO [3].

Results and Discussion

The valence states of Ce and Ni were examined by Ce L$_{III}$-edge and Ni K-edge XANES, respectively. CeO$_2$ with Ce^{4+} showed two XANES peaks at 5731.1 and 5738.0 eV as shown in Figure 1 (A), while a sharp peak at 5726.6 eV was observed for CeCl$_3$ with Ce^{3+}. The Ce L$_{III}$-edge XANES spectra of NCT and Ni/NCT were very close to that of CeCl$_3$, with a sharp peak at 5726.3 eV, and remained unchanged after catalytic tests. These indicated that Ce^{3+} species predominated in the prepared catalysts and were quite stable under the SRM reaction conditions.

Ni K-edge EXAFS suggested the local coordination structure of the supported Ni species on Ni/NCT. Fresh Ni/NCT exhibited the similar Ni K-edge XANES to that of Ni foil, as shown in Figure 1 (B). The contribution of Ni-Ni at 0.248 ± 0.001 nm was observed on the fresh Ni/NCT, and the coordination number (CN) of the Ni-Ni bond was estimated to be 9.9 ± 1.1 (Table 1), indicating that the supported Ni species were metallic on NCT.

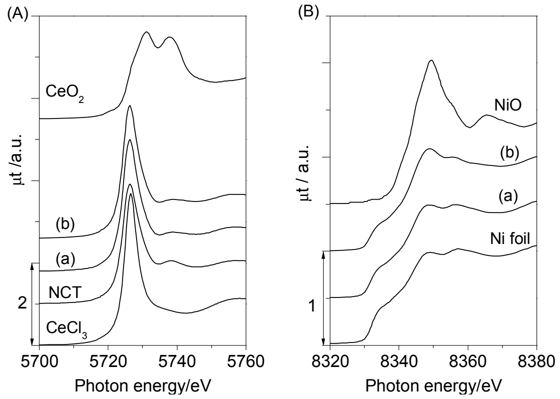

Figure 1 (A) Ce L$_{III}$-edge and (B) Ni K-edge XANES spectra of the Ni/NCT catalysts. (a) Fresh 4 wt% Ni/NCT and (b) used 4 wt% Ni/NCT.

After SRM reaction, the white-line intensity of the used Ni/NCT catalyst at the Ni K-edge XANES increased a little (Figure 1 (B)), implying the slight oxidation of Ni particles under the SRM reaction conditions. While Ni K-edge EXAFS Fourier transform was successfully fitted with Ni-Ni at 0.249 ± 0.001 nm (CN = 10.5 ± 0.5), and the contribution from NiO was negligible as shown in Table 1. These results suggested that metallic Ni dominated in the Ni/NCT catalysts with surface Ni species oxidized by steam under the reaction conditions.

Table 1: Curve fitting results of Ni K-edge EXAFS (R = 0.10- 0.30 nm)

Samples	Shell	CN	Distance /nm	σ^2 /× 10^{-5} nm^2
fresh	Ni-Ni	9.9 ± 1.1	0.248 ± 0.001	6 ± 1
used	Ni-Ni	10.5 ± 0.5	0.249 ± 0.001	5 ± 1

References

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