XAFS Characterization of Ni/NaCeTi_2O_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_2O_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_2O/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. 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.

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)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Shell</th>
<th>CN</th>
<th>Distance /nm</th>
<th>σ^2 /× 10^{-5} nm^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>fresh</td>
<td>Ni-Ni</td>
<td>9.9 ± 1.1</td>
<td>0.248 ± 0.001</td>
<td>6 ± 1</td>
</tr>
<tr>
<td>used</td>
<td>Ni-Ni</td>
<td>10.5 ± 0.5</td>
<td>0.249 ± 0.001</td>
<td>5 ± 1</td>
</tr>
</tbody>
</table>

References

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