

Ni-supported $\text{Ce}_2\text{Zr}_2\text{O}_x$ ($x = 7-8$) Catalysts for CH_4 Steam Reforming

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Introduction

$\text{Ce}_2\text{Zr}_2\text{O}_x$ ($x = 7-8$) was prepared for a support for automobile exhausting catalyst¹, and we have found that Ni-supported $\text{Ce}_2\text{Zr}_2\text{O}_x$ was efficient for methane steam reforming reaction to produce H_2 and CO at $\text{H}_2\text{O}/\text{CH}_4=1$. The catalytic performance of $\text{NiO}_y/\text{Ce}_2\text{Zr}_2\text{O}_x$ ($x=7-8$) strongly depended on the phase and oxygen content (x) of $\text{Ce}_2\text{Zr}_2\text{O}_x$, showing a unique discontinuity in catalytic activity at $x=7.5$. The oxidation states and local coordination structures of Ni and Ce species on the catalysts were investigated by Ni K-edge and Ce L_{III}-edge XAFS analysis.

Experimental

Ordered $\text{Ce}_2\text{Zr}_2\text{O}_7$ solid solution (Ce/Zr=1/1 molar ratio)¹ was prepared by co-precipitation using an aqueous NH_3 solution of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, followed by reduction with CO at 1673 K. The sample was calcined at 773 K and impregnated with an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, followed by calcination. $\text{Ni}/\text{Ce}_2\text{Zr}_2\text{O}_7$ was prepared by the reduction of $\text{NiO}/\text{Ce}_2\text{Zr}_2\text{O}_8$ with H_2 at 773 K.

XAFS spectra were measured at 293 K at BL-9A (Ce L_{III}-edge) and BL-12C (Ni K-edge) with Si(111) channel-cut crystals monochromator. Ni K-edge XAFS was measured in fluorescence mode, and fluorescent X-rays were detected by a Lytle detector filled with Ar, while incident X-rays were detected by an ionization chamber filled with N_2 . Ce L_{III}-edge XANES was measured in transmission mode, and incident and transmitted X-rays were detected by ionization chambers filled with N_2 (30%) + He (70%) and N_2 , respectively.

Results and Discussion

Methane steam reforming activity highly depended to the amount of oxygen (x) in $\text{Ce}_2\text{Zr}_2\text{O}_x$ and $\text{NiO}_y/\text{Ce}_2\text{Zr}_2\text{O}_x$ ($x < 7.5$) showed significant activity for the reaction. Figure 1 (A) shows the Ce L_{III}-edge XANES spectra of $\text{NiO}_y/\text{Ce}_2\text{Zr}_2\text{O}_x$ samples. $\text{Ni}/\text{Ce}_2\text{Zr}_2\text{O}_7$, which was active for CH_4 steam reforming, showed no change in its XANES spectra before or after the CH_4 steam reforming at 923 K. Ce L_{III}-edge XANES data revealed that $\text{NiO}_y/\text{Ce}_2\text{Zr}_2\text{O}_{7.4}$ was reduced to $\text{Ce}_2\text{Zr}_2\text{O}_7$ after the CH_4 steam reforming. In contrast, there was no significant

changes Ce L_{III}-edge XANES spectrum of $\text{NiO}_y/\text{Ce}_2\text{Zr}_2\text{O}_{7.6}$ and $\text{NiO}/\text{Ce}_2\text{Zr}_2\text{O}_8$ after CH_4 steam reforming. Thus, it was indicated that active $\text{NiO}_y/\text{Ce}_2\text{Zr}_2\text{O}_x$ ($x < 7.5$) catalysts converted to $\text{Ni}/\text{Ce}_2\text{Zr}_2\text{O}_7$ under the CH_4 steam reforming conditions.

The oxidation states and local coordination structures of the supported Ni species were investigated by Ni K-edge XANES and EXAFS. Similar changes in the XANES spectra of $\text{NiO}_y/\text{Ce}_2\text{Zr}_2\text{O}_x$ ($x < 7.5$) were observed at Ni K-edge before and after the CH_4 steam reforming (Figure 1 (B)). Ni species on the active phases converted to metallic Ni species, while oxidized Ni species on inactive phases did not change under the reaction conditions. The curve-fitting analysis of Ni K-edge EXAFS of $\text{Ni}/\text{Ce}_2\text{Zr}_2\text{O}_7$ suggested that the Ni nanoparticles were metallic Ni species, whose Ni-Ni coordination number was 11.1 ± 1.3 at 0.249 ± 0.001 nm.

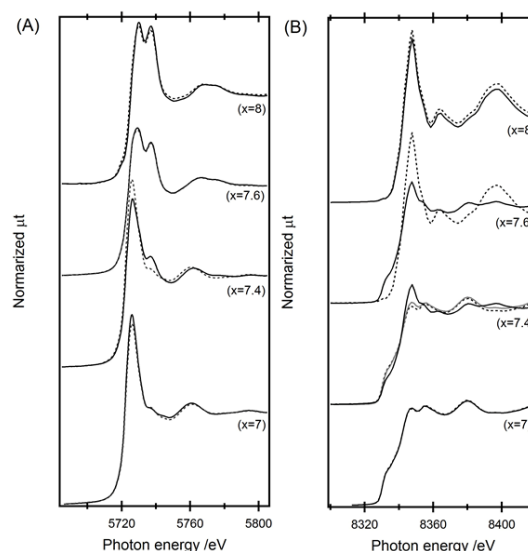


Figure 1. (A) Ce L_{III}-edge and (B) Ni K-edge XANES spectra of $\text{NiO}_y/\text{Ce}_2\text{Zr}_2\text{O}_x$ catalysts before and after the CH_4 steam reforming.

Reference

[1] A. Suda, Y. Ukyo, H. Sobukawa, M. Sugiura, *J. Ceram. Soc. Jpn.* **2002**, *110*, 126.

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