Ni-supported Ce₂Zr₂Oₓ (x = 7-8) Catalysts for CH₄ Steam Reforming

Mizuki TADA*¹, Nozomu ISHIGURO¹,², Jun-ichi SOGA², Shenghong ZHANG¹, Yasuhiro IWASAWA²

¹ Institute for Molecular Science, Myodaiji, Okazaki, Aichi 444-8585, Japan.
² Department of Chemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan.

Introduction

Ce₂Zr₂Oₓ (x = 7-8) was prepared for a support for automobile exhausting catalyst¹, and we have found that Ni-supported Ce₂Zr₂Oₓ was efficient for methane steam reforming reaction to produce H₂ and CO at H₂O/CH₄=1. The catalytic performance of NiOy/Ce₂Zr₂Oₓ (x=7-8) strongly depended on the phase and oxygen content (x) of Ce₂Zr₂Oₓ, 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 LIII-edge XAFS analysis.

Experimental

Ordered Ce₂Zr₂O₇ solid solution (Ce/Zr=1/1 molar ratio)¹ was prepared by co-precipitation using an aqueous NH₃ solution of Ce(NO₃)₃·6H₂O and ZrO(NO₃)₂·2H₂O, followed by reduction with CO at 1673 K. The sample was calcined at 773 K and impregnated with an aqueous solution of Ni(NO₃)₂·6H₂O, followed by calcination. Ni/Ce₂Zr₂O₇ was prepared by the reduction of NiOy/Ce₂Zr₂O₈ with H₂ at 773 K.

XAFS spectra were measured at 293 K at BL-9A (Ce LIII-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 N₂. Ce LIII-edge XANES was measured in transmission mode, and incident and transmitted X-rays were detected by ionization chambers filled with N₂ (30%) + He (70%) and N₂, respectively.

Results and Discussion

Methane steam reforming activity highly depended to the amount of oxygen (x) in Ce₂Zr₂Oₓ and NiOy/Ce₂Zr₂Oₓ (x<7.5) showed significant activity for the reaction. Figure 1 (A) shows the Ce LIII-edge XANES spectra of NiOy/Ce₂Zr₂Oₓ samples. Ni/Ce₂Zr₂O₇, which was active for CH₄ steam reforming, showed no change in its XANES spectra before or after the CH₄ steam reforming at 923 K. Ce LIII-edge XANES data revealed that NiOy/Ce₂Zr₂O₇₄ was reduced to Ce₂Zr₂O₇ after the CH₄ steam reforming. In contrast, there was no significant changes Ce LIII-edge XANES spectrum of NiOy/Ce₂Zr₂O₂₆ and NiO/Ce₂Zr₂O₈ after CH₄ steam reforming. Thus, it was indicated that active NiOy/Ce₂Zr₂Oₓ (x<7.5) catalysts converted to Ni/Ce₂Zr₂O₇ under the CH₄ 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 NiOy/Ce₂Zr₂Oₓ (x<7.5) were observed at Ni K-edge before and after the CH₄ 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 Ni/Ce₂Zr₂O₇ 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.

Reference


* mtada@ims.ac.jp