

Reduction Property of NiO Species on Metallic Ni Core under CH₄ AtmosphereYusaku YAMAMOTO*, Hitoe NONOBE, Shunsuke OSAKA,
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1 Introduction

The supported Ni particles are widely used as catalysts for dry and steam reforming reaction of methane. Under catalytic reaction conditions, the Ni species is exposed by the oxidative and reductive molecules including in the reactants and products gases. The chemical state conversion of the Ni species may be caused by the reaction with those molecules, and it affects the catalytic activity. The redox property of the Ni species located at the particle surface is important for catalyst design, because the catalytic reaction is proceeded at the particle surface. The purpose of this research is to clarify the reduction property of the NiO species located at the surface of metallic Ni particles under the CH₄ atmosphere.

2 Experiment

The SiO₂-supported Ni catalyst (5 wt%) was prepared by the impregnation method using aqueous solution of Ni(NO₃)₂. The stoichiometric amount of citric acid relative to Ni²⁺ was added in the precursor solution to control the Ni particle size. The average Ni particle size was determined to be 3 nm by the TEM observation.

The *in-situ* XAFS measurements using the flow-type cell made of SiO₂ glass was performed at BL-9C station of PF (KEK). The surface of the Ni(0) particle was oxidized by the O₂ exposure at room temperature [1,2]. After that, the chemical state analysis on the Ni species was performed during the temperature-programmed reduction (TPR) process under the 10 vol% CH₄/He gas flow (100 cm³/min).

3 Results and Discussion

The metallic Ni particle generated by the reduction with H₂ was exposed to the O₂ environment at room temperature, and the fraction of NiO was estimated to be 45% by the linear combination fitting analysis based on the XANES spectrum. The thickness of the surface NiO layer was calculated as *ca.* 3 Å based on the fraction of NiO and the particle size. It was suggested that the single surface layer of the Ni particle was locally oxidized [1,2].

Figure 1 shows the composition changes of the Ni species during the TPR process. The surface NiO species on the metallic Ni core was reduced at 300 °C by CH₄. It is *ca.* 200 °C lower than the reduction temperature of NiO particles under the CH₄ atmosphere. Under the H₂ atmosphere, the NiO species located on the metallic Ni core is reduced at much lower temperature of around 120 °C. These results indicate that the NiO species located on the metallic Ni core has an excellent ability to release

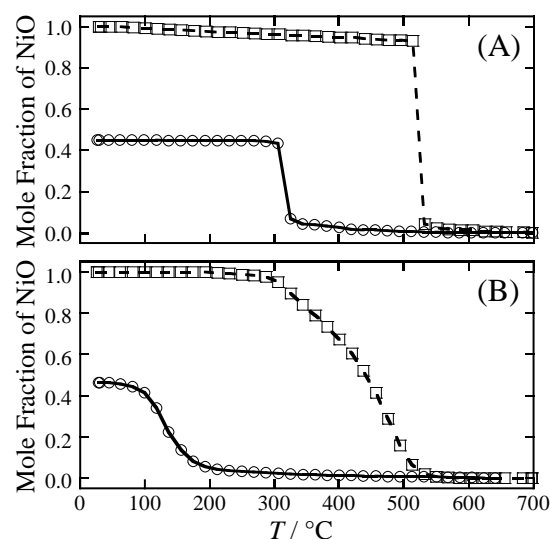


Fig. 1: The temperature changes of NiO fraction during the TPR process under CH₄ (A) and H₂ (B) atmosphere. The solid lines and dashed lines show the reduction of NiO species on metallic Ni core and NiO particle, respectively.

the oxide ion. In addition, the Ni particle surface is easily oxidized under the mild condition such as room temperature. It is expected that these unique characteristics promote the catalytic reactions driven by the redox reactions of the active Ni particles.

The reduction of NiO by CH₄ was proceeded at higher temperature (*ca.* 520 °C) than by H₂ indicating the lower reducibility of CH₄. It was remarkable that the reduction of NiO under CH₄ was rapidly completed at that temperature, which was contrast to the corresponding process under H₂. At the beginning of the reduction of NiO by CH₄, the generated Ni(0) species drives the catalytic CH₄ decomposition to generate the H₂ molecules, which can enhance the reduction of remaining NiO.

References

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