

XAFS Analysis of Ni Catalyst Supported on SiO<sub>2</sub>-covered  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

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## 1 Introduction

The Ni species supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> easily converts to NiAl<sub>2</sub>O<sub>4</sub> and its formation is one of the reasons of the catalytic deactivation [1]. On the other hand, our previous chemical state analysis of Ni catalysts has been clarified that the stable NiO species is generated on SiO<sub>2</sub> by the treatment under an oxidative environment at elevated temperature [2]. In this study, the XAFS analysis of the supported Ni species on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particles, which surface is covered by SiO<sub>2</sub>, has been carried out to evaluate the influence of the surface chemical species of the supporting material. Such SiO<sub>2</sub>-covered  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (SiO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) was prepared by the chemical modification technique for the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and the Ni species was supported by the impregnation method. The purpose of this study is to clarify the chemical state variation of the supported Ni species of Ni/SiO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in comparison to those of Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni/SiO<sub>2</sub>.

## 2 Experiment

To prepare SiO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the surface activated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by the reflux in hydrochloric acid for 6 h at 115 °C was mixed with triethyl octyl orthosilicate, and the suspended solution in toluene was refluxed for 48 h at 120 °C. The obtained powder was filtrated, dried under vacuum for 10 h at 110 °C, and subjected to the calcination in air for 5 h at 850 °C. All supported Ni catalysts were prepared using aqueous solution of nickel nitrate by the standard impregnation method, and were calcined in air for 3 h at 600 °C.

The X-ray absorption fine structure (XAFS) measurements were carried out at BL-9C of the Photon Factory (KEK). The *in-situ* XAFS measurements were performed during the temperature-programmed reduction (TPR) by H<sub>2</sub> and oxidation (TPO) by O<sub>2</sub> from room temperature to 900 °C. The gas atmosphere was switched at room temperature.

## 3 Results and Discussion

The XANES spectral change during the TPR process of Ni/SiO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was shown in Fig. 1. The initial spectrum of both catalysts suggested the mixture of NiAl<sub>2</sub>O<sub>4</sub> and NiO, indicating that the stable NiAl<sub>2</sub>O<sub>4</sub> species was generated by the calcination procedure in air. The final spectrum was in agreement with that of Ni foil, and it was revealed that both NiAl<sub>2</sub>O<sub>4</sub> and NiO species were reduced by H<sub>2</sub> to form the metallic Ni particles. The value of X-ray absorbance at the initial white-line peak top was plotted in Fig. 1(c) as a function of temperature. It was found that the reduction of NiAl<sub>2</sub>O<sub>4</sub> and NiO started at *ca.* 700 °C on both SiO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and that the reduction

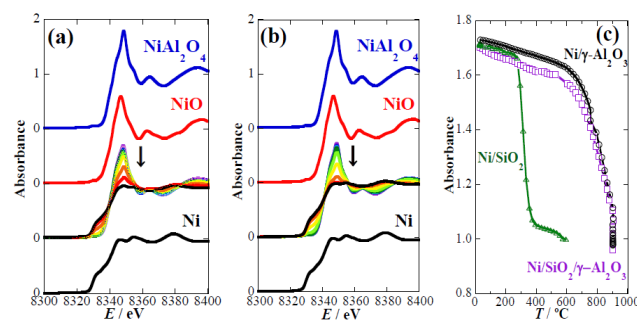


Fig. 1: XANES spectral change of Ni/SiO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (a) and Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (b) during the TPR process. The change of X-ray absorbance is plotted versus temperature for the Ni/SiO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni/SiO<sub>2</sub> in (c).

temperature was remarkably increased by *ca.* 400 °C in comparison to NiO supported on SiO<sub>2</sub>.

The XANES spectral change during the TPO process of the Ni/SiO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and the changes of X-ray absorbance are given in Fig. 2. A clear spectral change from metallic Ni to NiO was observed by the TPO procedure. Both the complete agreement of the final spectrum with NiO and the similar oxidation temperature to Ni/SiO<sub>2</sub> indicates that the formation of catalytically inactive NiAl<sub>2</sub>O<sub>4</sub> is suppressed by the surface coverage of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with SiO<sub>2</sub>.

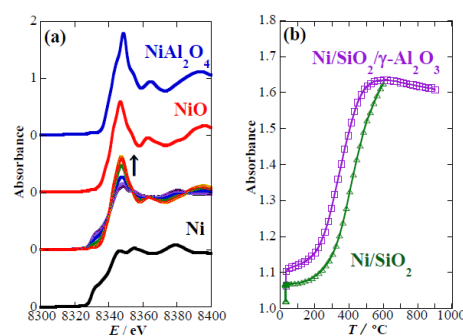


Fig. 2: XANES spectral change (a) and the X-ray absorbance change as a function of temperature (b) of Ni/SiO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> during the TPO process. In (b), the absorbance change is compared with that of Ni/SiO<sub>2</sub>.

## References

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