

# XAFS Analysis on Reduction Process of Ni Supported on Rutile TiO<sub>2</sub>

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The effect of the calcination and reduction treatment on the chemical state of the Ni species supported on TiO<sub>2</sub> was revealed by the XRD and XAFS method. The TiO<sub>2</sub>-supported Ni catalyst calcined at various temperatures was characterized by the XRD measurements. It is revealed that the NiO species was incorporated into TiO<sub>2</sub> support as the species of NiTiO<sub>3</sub>, when the calcination temperature was higher than 600 °C. The chemical state conversion of the Ni species during the temperature programmed reduction process was investigated by *in situ* XAFS measurements. The reduction of NiTiO<sub>3</sub> proceeded below 700 °C, and the metallic Ni(0) species was generated on TiO<sub>2</sub>. The reduction temperature was higher than that of NiO on TiO<sub>2</sub>.

## 1. Introduction

The active metal species supported on chemically stable materials such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> are widely used in various applications, such as synthesis of organic substances and environmental purification. One of the useful catalysis reactions is the water gas shift (WGS) reaction, and it is important for industrial application for the operation of fuel cell (FC), because this reaction converts CO to CO<sub>2</sub> and generates H<sub>2</sub> from water. TiO<sub>2</sub>-supported Au catalyst shows the high catalytic activity for the WGS reaction [1]. However, because of the demand to reduce the cost for the operation, the alternative catalysts are highly required to achieve the practical utilization of the FC system. The Ni catalyst is attracting attentions as the alternative materials for the noble metal catalyst. It has been reported that the Ni catalyst supported on TiO<sub>2</sub> has high catalytic activity for the WGS reaction of CO [2]. In this case, it is believed that the strong metal-support interaction plays important role for the catalytic performance.

The X-ray absorption fine structure (XAFS) spectroscopy is one of the most powerful techniques for the chemical state analysis of supported metal catalysts. In our previous researches, the chemical state conversion of the Ni species supported on SiO<sub>2</sub> was investigated by *in situ* XAFS measurements during the temperature-programmed reduction (TPR) process [3-5]. The reduction of NiO was driven at two different temperature regions. The Ni(II) species reduced at higher temperature is stabilized by the SiO<sub>2</sub> supports at the interface between the NiO particle and the SiO<sub>2</sub> surface. According to the extended X-ray absorption fine structure (EXAFS) analysis, it has been clarified that the Ni-O bond distance for the remaining Ni(II) species at high temperature during the TPR process is shorter than that of standard NiO species, and it is suggested that the Ni<sub>2</sub>SiO<sub>4</sub> like structure is generated

to stabilize the Ni(II) species at the SiO<sub>2</sub> surface.

There has been a great discussion about the effect of the support material on the performance of catalysis reactions. One of the most important effects is the formation of a complex oxide of the supporting material with the active metal species. In the case of the Ni species, the supporting material of TiO<sub>2</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> may form NiTiO<sub>3</sub> and NiAl<sub>2</sub>O<sub>4</sub>, respectively [6,7]. It is important for the catalysis design to understand the formation and its chemical state conversion of such complex oxides, because the aggregation of the active metal species can be prevented by the formation of such complex oxides under the reaction conditions. The present study has been carried out to reveal the chemical state and the reduction property of TiO<sub>2</sub>-supported Ni catalyst formed by the calcination at various temperatures.

## 2. Experimental

TiO<sub>2</sub>-supported Ni catalyst was prepared by the conventional impregnation method with the Ni loading of 5 wt%. The TiO<sub>2</sub> powder (rutile type) was suspended in an aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and the mixture was stirred for 1 h at 70 °C. The mixture was dried at 70 °C for 72 h in air, and the obtained powder was calcined for 3 h at 300 °C, 600 °C, 700 °C, 800 °C, and 900 °C in air.

The X-ray diffraction (XRD) measurements were performed with Ultima IV diffractometer (Rigaku, Japan) equipped with a linear detector using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The diffraction intensities were recorded over the  $2\theta$  range between 10° and 80°.

The *in situ* XAFS measurements were carried out at BL-3 of the SR Center (Ritsumeikan University) and BL-12C of the Photon Factory (High Energy Accelerator Research Organization: KEK) at the Ni K edge in the transmission mode. The Si(220) double-crystal monochromator was used at BL-3 of SR center. The higher-order harmonics were removed by detuning the Si(111) double-crystal

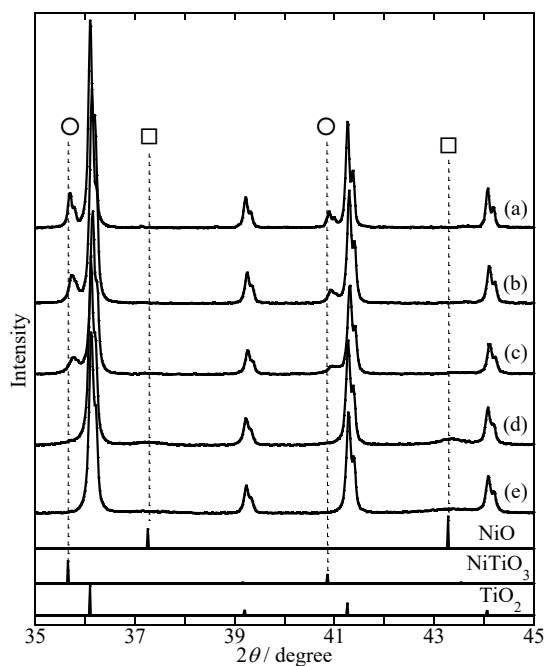
monochromator for the XAFS measurements at the BL-12C of Photon Factory. The measurement time was 1 min for each XAFS spectrum. The XAFS spectra were recorded during the TPR process for the calcined Ni catalyst supported on TiO<sub>2</sub>. The sample powder was set in a flow-type *in situ* XAFS cell made of SiO<sub>2</sub> glass, and was heated from room temperature to 900 °C with the heating rate of 10 °C/min under the dilute H<sub>2</sub> gas flow (10 vol% balanced by He) with the flow rate of 100 cm<sup>3</sup>/min.

### 3. Results and Discussion

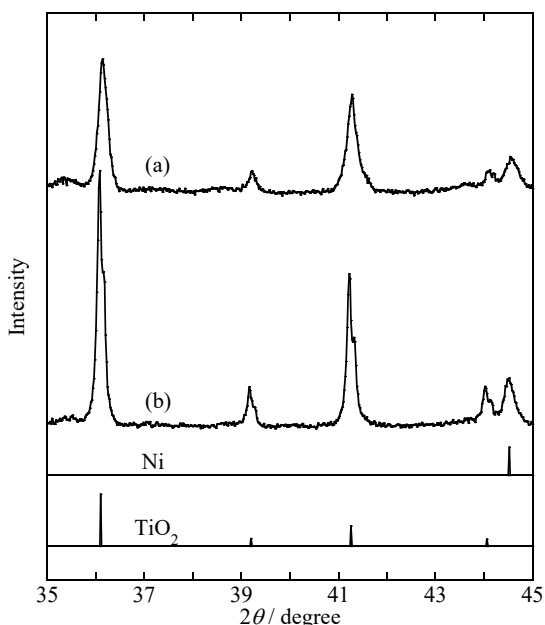
The observed XRD patterns of TiO<sub>2</sub>-supported Ni catalysts after the calcination at various temperatures are shown in Fig. 1. In all XRD patterns, the diffraction lines derived from rutile TiO<sub>2</sub> were observed, and the crystal structure of rutile TiO<sub>2</sub> was remained by the impregnation process and the following calcination process. There are diffraction lines at 37.25° and 43.27° in the XRD patterns of TiO<sub>2</sub>-supported Ni catalysts calcined at 300 °C and 600 °C. These diffraction lines are assigned to the 111 (37.25°) and 200 (43.27°) reflection of NiO. On the other hand, there is no diffraction lines derived from NiO in the XRD patterns of samples calcined at 700 °C and higher. Moreover, the diffraction lines assigned to NiTiO<sub>3</sub> appeared and became sharp with the increase in the calcination temperature. The decomposition of Ni(NO<sub>3</sub>)<sub>2</sub> occurred during the calcination process at below 600 °C, and the NiO crystallite was generated on rutile TiO<sub>2</sub>. After that, the NiO species was changed to NiTiO<sub>3</sub> when the calcination temperature was above 700 °C. These results indicate that the calcination temperature is important to control the chemical state of the Ni species on TiO<sub>2</sub>.

The TiO<sub>2</sub>-supported Ni catalysts calcined at 300 °C and 900 °C were reduced by H<sub>2</sub> at 900 °C for 3 h. The XRD patterns after the reduction treatment are given in Fig. 2. The diffraction lines of NiO and NiTiO<sub>3</sub> disappeared for both samples. On the other hand, the diffraction line at 44.51° appeared, and it was found that the metallic Ni(0) species was formed on TiO<sub>2</sub>. It should be noted that not only NiO but also NiTiO<sub>3</sub> was reduced to the metallic Ni(0) species. This result suggests the emission of the incorporated Ni(II) species in TiO<sub>2</sub> as NiTiO<sub>3</sub> by the reduction treatment at 900 °C.

The XANES spectral changes of the Ni species supported on TiO<sub>2</sub> during the TPR processes are shown in Fig. 3. As discussed in the previous section on the XRD patterns, the initial Ni(II) species of these samples is NiO (300 °C) and NiTiO<sub>3</sub> (900 °C), respectively, and thus the initial XANES spectra were consistent each other. The NiTiO<sub>3</sub> shows the broader white line with the shoulder structure at the higher energy side and the slight edge shift to the



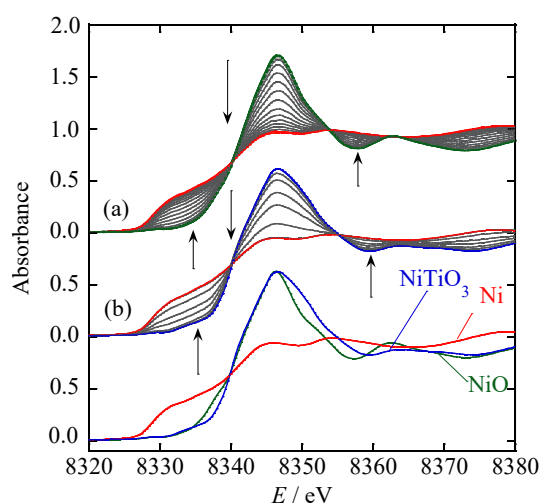
**Fig. 1** XRD patterns of TiO<sub>2</sub>-supported Ni catalysts after the calcination at various temperatures. The calcination temperature was 900 °C (a), 800 °C (b), 700 °C (c), 600 °C (d), and 300 °C (e). The diffraction line of NiO and NiTiO<sub>3</sub> are labeled by □ and ○, respectively. The reference data for NiO, NiTiO<sub>3</sub>, and TiO<sub>2</sub> are included for comparison.



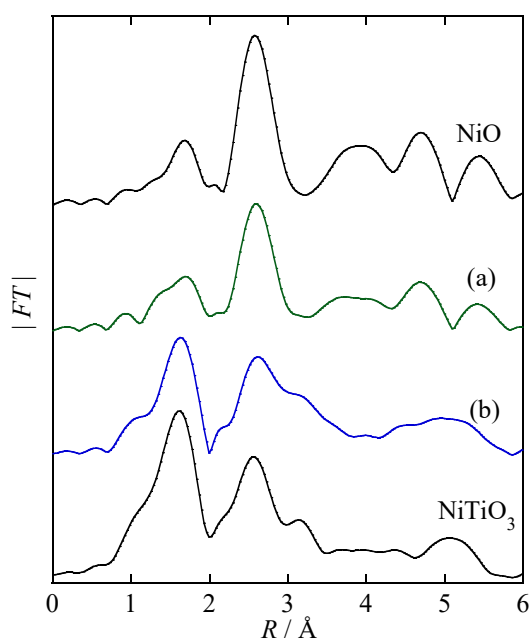
**Fig. 2** XRD patterns of TiO<sub>2</sub>-supported Ni catalysts after the reduction treatment at 900 °C. Samples were calcined at 300 °C (a) and 900 °C (b) prior to the reduction treatment. The reference data for Ni metal and TiO<sub>2</sub> are included for comparison.

lower energy side (8341 eV). The Fourier transform functions of the initial spectra are compared in Fig. 4 with those of the reference powders of NiO and NiTiO<sub>3</sub>, and it also supports the formation of NiO (calcination at 300 °C) and NiTiO<sub>3</sub> (calcination at 900 °C).

For both samples, Fig. 3 clearly indicates that the final XANES spectra are in agreement with the metallic Ni(0) species. Therefore, both the NiO and



**Fig. 3** XANES spectral change of TiO<sub>2</sub>-supported Ni catalysts calcined at 300 °C (a) and 900 °C (b) during the TPR process under H<sub>2</sub> atmosphere.

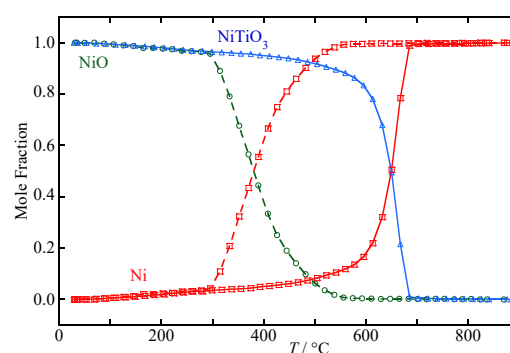


**Fig. 4** The Fourier transform functions of initial state of TiO<sub>2</sub>-supported Ni catalysts calcined at 300 °C (a) and 900 °C (b).

NiTiO<sub>3</sub> species are quantitatively reduced to Ni(0) after the reduction treatment at 900 °C. In addition, some isosbestic points observed clearly indicates that the conversion from NiO or NiTiO<sub>3</sub> to Ni(0) proceeds without any other metastable intermediate states.

The composition of the Ni species was analyzed by the linear combination fitting analysis based on the observed XANES spectrum by referring the XANES spectra of NiO, NiTiO<sub>3</sub>, and Ni metal. Figure 6 shows the composition changes during the TPR process for the TiO<sub>2</sub>-supported Ni catalysts calcined at 300 °C and 900 °C. The NiO species supported on TiO<sub>2</sub> was reduced at the temperature range between 300 °C and 500 °C. This reduction temperature agrees with that of the NiO species supported on SiO<sub>2</sub> [3-5]. Because the particle size was not very small for the present catalyst on TiO<sub>2</sub>, the stabilization at the interface on the TiO<sub>2</sub> surface was unclear and only the slight tailing was observed at over 450 °C.

On the other hand, the reduction temperature of the NiTiO<sub>3</sub> species was by 250 °C higher than that of NiO, and the reduction occurred at the temperature range between 600 °C and 700 °C. The higher reduction temperature indicates that the formation of the complex oxide with TiO<sub>2</sub> increases the resistance for the reduction of the Ni(II) species. In other words, the Ni(II) ion in NiTiO<sub>3</sub> is more stable against the reduction than that in NiO. It means that the sintering of the Ni(II) species to generate the large particle is also inhibited by the fixation of the Ni(II) ion in the TiO<sub>2</sub> matrix. The composition change from NiTiO<sub>3</sub> to Ni(0) shows the minor change at the lower temperature region than 600 °C. Because the atomic vibration affects to the XANES spectrum, and the



**Fig. 5** The composition changes of Ni species supported on TiO<sub>2</sub> during the TPR process. The broken lines and solid lines show the TiO<sub>2</sub> supported Ni catalyst calcined at 300 °C and 900 °C, respectively.

slight modification is frequently observed at the elevated temperatures. The composition analysis based on the XANES spectrum should be influenced by such slight modification of the XANES spectrum.

#### 4. Conclusions

In the present study, the chemical state conversion of the Ni species supported on TiO<sub>2</sub> has been investigated by *in situ* XAFS measurements. It is evaluated that the calcination temperature affects the chemical state of the supported Ni species. The NiO species was formed on TiO<sub>2</sub> in the Ni catalysts calcined at 300 °C and 600 °C, whereas the NiO species was incorporated into the TiO<sub>2</sub> lattice to form the NiTiO<sub>3</sub> species above 700 °C. The formed NiTiO<sub>3</sub> species was perfectly reduced to metallic Ni(0) by the reduction treatment under H<sub>2</sub> at 900 °C. However, the reduction temperature of NiTiO<sub>3</sub> was by 250 °C higher than that of NiO. This result indicates that the formation of the complex oxide increases the resistance for the reduction of the Ni(II) species and its aggregation.

#### Acknowledgement

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