Oxidation Reaction of Ni Particle with Heterogeneous Distribution for Oxidation State of Ni

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The oxidation reaction of SiO_2-supported Ni particles with the heterogeneous distribution of the oxidation state of Ni has been investigated by means of the *in-situ* XAFS technique. The temperature-programmed reduction of NiO was terminated to produce the mixed oxidation states of NiO and Ni(0) in a single particle. The amount of the Ni(0) species located at the particle surface was determined by the composition analysis using the XANES spectra of the partially reduced NiO particles measured before and after the O_2 exposure at room temperature. The oxidized fraction was apparently smaller than the pre-reduced Ni(0), indicating that the reduction of NiO begins at the specific surface site and the reduced region expands toward the particle core by digging into the particle. The O_2 exposure to the partially reduced NiO particle at room temperature generated the Ni(0) core surrounded by NiO.

1. Introduction

The supported Ni particle is widely used as catalysts for the dry and steam reforming reactions, the CH_4 decomposition reaction, and the partial oxidation reaction of CH_4. The Ni catalyst is investigated and developed as an alternate of noble metal catalysts. Under reaction conditions, supported Ni species is exposed by the reactive gasses including in the reactants and the products. The chemical state of Ni may be converted by the reaction with those gasses. Because the chemical state of the Ni species directly affects the catalytic performance, its analysis of the Ni species under the reaction conditions is necessary to design the catalyst with the improved performance.

X-ray absorption fine structure (XAFS) technique is one of the powerful tools for the chemical state analysis of the Ni species supported on SiO_2 under the reaction gas environment. The XAFS spectrum provides the knowledge of the electronic state and the local structure of a target element, and *in-situ* measurement is available under heating and gas flow conditions in the case of the measurements using the hard X-ray at the K edge of the 3d transition metal elements. The previous *in-situ* XAFS study revealed the chemical state conversion of the supported Co [1], Ni [2], and Cu [3] species during the temperature-programmed reduction (TPR) and oxidation (TPO) processes using H_2 and O_2 as the most basic reductant and oxidant, respectively.

It has been clarified that the metallic Ni(0) particle supported on SiO_2 suffers the surface oxidation by the O_2 exposure at room temperature [2]. The oxidized amount is in excellent agreement with the expectation based on the particle size under an assumption that only the surface layer (about 1 or 2 atomic layer) of the Ni(0) particle has been oxidized. The oxidation temperature of the remaining part, *i.e.*, the Ni(0) core surrounded by the surface NiO layer,

is increased with increasing the particle size [4], suggesting that the oxidation reaction proceeds from the outer layer to the inner core of the particle.

The reduction of NiO located at the particle surface of Ni(0) is completed at below 200 °C, and it is lower than that of the reduction of NiO particles [5], which occurs at above 300 °C. This fact indicates that the surface NiO species existed on metallic Ni(0) core has an excellent ability to release oxide ion. On the other hand, the reduction of NiO proceeds in two steps at around 350 °C and 600 °C under the H_2 atmosphere. The different reduction temperatures are explained by the existence of two types of NiO with the different stability. The NiO species existed at an interface between the NiO particle and SiO_2 is stabilized by the interaction with the SiO_2 surfaces, and thus such NiO is reduced at higher temperature than the other NiO without any interactions with SiO_2. This implies that the interface NiO can act as an anchor to prevent the migration of the particles.

The particle size dependence of the amount of NiO, *i.e.*, the surface NiO with the Ni(0) core appeared in the TPO process of Ni(0) and the interface NiO of the Ni(0) particle appeared in the TPR process of NiO, has demonstrated that such the heterogeneous distribution of the chemical state of Ni is appeared in
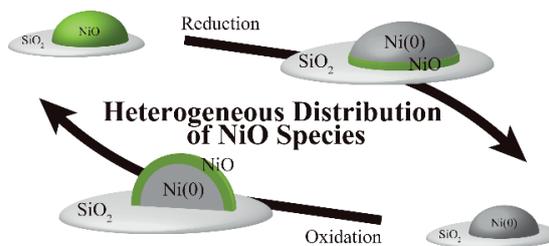
Fig. 1 The heterogeneous distribution of chemical state of Ni in a single particle supported on SiO_2 during the TPR and TPO processes.

a single particle as shown in Fig. 1. The highly oxidizing ability of the surface NiO and the ability to prevent the particle migration of the interface NiO can provide new functions to the supported Ni catalyst. If we could control actively the existence of such the heterogeneous distribution, the knowledge will become a significant guideline to improve the catalysis performance for the practical utilization of the Ni catalysts.

As seen in Fig. 1, the interface NiO connects the Ni(0) particle with SiO$_2$ and such the mixed oxidation state of Ni is generated during the TPR process of NiO. Here, it is implied that the surface NiO and the interface NiO can be coexisted in a single particle, if such the Ni(0) particle with the interface NiO is exposed to the O$_2$ atmosphere at room temperature. In addition, it is possible that the amount of the Ni(0) part is controlled by changing the termination temperature of the TPR process. The evaluation of the reduction temperature of the surface NiO containing the Ni(0) core and its dependence on the amount of the Ni(0) part will become useful to understand the oxidizing ability of the surface NiO to utilize it as the catalyst for oxidation reactions. In this study, the TPR processes have been observed by *in-situ* XAFS measurements at the Ni K edge for the Ni particles with heterogeneous distribution of Ni(0) and NiO.

2. Experimental

The SiO$_2$-supported Ni catalysts were prepared by the impregnation method by adding malonic acid to control the particle size. The stoichiometric amount of malonic acid was added into the precursor solution of nickel(II) nitrate. The mixture of the solution and SiO$_2$ powder was dried, calcined in air, and reduced under the flow of H$_2$. The Ni loading was set to be 5 wt%. The particle size was estimated to be 6 nm by the TEM observations.

The *in-situ* XAFS measurements were performed by the transmission mode at BL-3 of the SR center (Ritsumeikan University) and BL-9C of Photon Factory (High Energy Accelerator Research Organization). The sample powder was set in a flow-type *in-situ* XAFS cell made of SiO$_2$ glass.

At first, the TPR process was carried out for the SiO$_2$-supported NiO catalyst using the flow-type *in-situ* XAFS cell under 10 vol% H$_2$ gas flow (100 cm^3/min) diluted by He. The temperature elevation was terminated at four different temperatures (334 °C, 427 °C, 435 °C, and 700 °C) to change the amount of generated Ni(0) (the pre-reduction treatment), and the cell was cooled down to room temperature. The flowing gas was switched from 10 vol% H$_2$/He to 10 vol% O$_2$/He at room temperature. The sample was again heated up to 600 °C with the heating rate of 10 °C/min under the dilute O$_2$ gas flow.

During this sequence of the gas and temperature treatments, the *in-situ* XAFS measurements were carried out at the Ni K edge.

3. Results and Discussion

Figure 2 shows the XANES spectra measured at room temperature after the pre-reduction treatment under H$_2$ atmosphere. All XANES spectra pass through the isosbestic points of the XANES spectra of the SiO$_2$-supported NiO and Ni(0) particle. Thus, the mole fractions of Ni(0) and NiO were estimated by the linear combination fitting (LCF) analysis based on XANES spectrum. The reduction temperatures and the percentage of the generated Ni(0) state are summarized in Table 1. The amount of Ni(0) was successfully changed between 9% and 100% by varying the termination temperature of the pre-reduction treatment. As discussed later, the fraction of the Ni species located at the particle surface is estimated to be 45% for the present sample with the average particle size of 6 nm. Thus, the 9% reduction (terminated at 334 °C) does not convert the whole surface, whereas the 64% reduction (terminated at 435 °C) exceeds the fraction of the surface Ni species. The intermediate 50% reduction
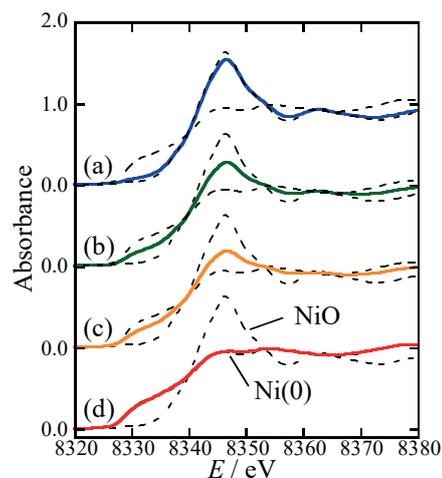
Fig. 2 XANES spectra of SiO$_2$-supported Ni particles reduced at several temperatures under H$_2$ atmosphere. The termination temperature of the pre-reduction treatment was 334 °C (a), 427 °C (b), 435 °C (c), and 700 °C (d).

Table 1. The heating conditions and the percentage of Ni(0) after the pre-reduction process.

Pre-reduction temperature / °C	Percentage of Ni(0) / %
700	100
435	64
427	50
334	9

almost corresponds to the fraction of the surface Ni species, if the reduction proceeds from the particle surface as in the case of the oxidation of Ni(0). This study has shown that it is possible to control the amount of Ni(0) in the NiO particle by the termination of the TPR process. It should be noted that the amount (percentage) of Ni(0) is changed by not only the termination temperature of the TPR process but also the particle size of NiO, because the reduction temperature of NiO is dependent on the particle size.

The XANES spectral change of the perfectly reduced sample is given in Figure 3 for the TPO process under the dilute O_2 atmosphere. The initial spectrum before the gas switch agrees with that of metallic Ni(0) reference. After the gas switch from H_2/He to O_2/He at room temperature, the X-ray absorbance of the white line peak of NiO at 8347 eV was immediately increased and the absorption edge energy was shifted to higher energy. The XANES change was explained by the partial oxidation of the Ni(0) particle. Based on the previous research [4], this change observed at room temperature is reasonably assigned to the surface oxidation of the Ni(0) particle. The fraction of the generated NiO was decided to be 45% by the LCF analysis of the XANES spectrum. The thickness of the surface NiO layer is estimated to 5 Å, which is almost comparable to the values reported previously [2,4].

In the same way, the surface oxidation was observed for all samples given in Table 1 and Fig. 2 with the different amount of Ni(0). Table 2 summarizes the mole fraction of the Ni(0) state before and after the gas switch at room temperature. The amount of the Ni species located at the particle
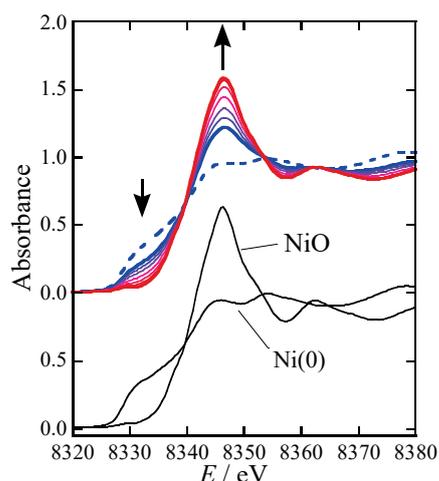
Table 2 The fraction of metallic Ni(0) species before and after the O_2 exposure at room temperature and their difference corresponding to the oxidized percentage.

Percentage of Ni(0)		
under H_2 / %	under O_2 / %	Oxidized by O_2 / %
100	55	45
64	37	27
50	29	21
9	3	6

surface was estimated as 45% according to the oxidized fraction of the perfectly reduced sample. For the other three samples, it was found that the oxidized fraction was lower than 45%. When we assume that the 9% reduction occurs at the particle surface of NiO, all the 9% Ni(0) is oxidized by the O_2 exposure, if only a part of such the Ni(0) state located on NiO is not highly stabilized against the oxidation. The same trend was observed for the 50% reduced sample. The oxidized fraction of 21% was apparently smaller than the previously reduced Ni(0), and 29% relative to all Ni still remains as Ni(0) after the O_2 exposure. Because this partial oxidation is considered to proceed at the particle surface, 29% of Ni(0) forms the Ni(0) core surrounded by NiO. In the case of the 64% reduced sample, the oxidized fraction (27%) was similarly small. These results indicate that the particle surface is not perfectly reduced by the partial reduction, *i.e.*, the Ni(0) species exists at not only the particle surface but also the inner part of the particle. It is thus considered that the reduction of NiO begins at the specific surface site and the reduced region expands towards the particle core by digging into the particle. The contact with O_2 at room temperature leads to the oxidation of only the exposed Ni(0) at the particle surface. As the result, the Ni(0) core surrounded by NiO is generated in the particle. On the contrary, it is thus impossible to form the NiO core covered by Ni(0).

The oxidation temperature of such the Ni(0) core surrounded by NiO has been analyzed by *in-situ* XAFS measurements for the succeeding TPO process under the O_2/He gas flow. As shown in Fig. 3, the white line peak was further grown, and the absorption edge was shifted to the higher energy side. The edge energy was finally consistent with that of reference NiO, indicating the completion of the conversion to NiO. The existence of some isosbestic points suggests the two-phase conversion from Ni(0) to NiO without any other metastable states.

The Ni(0) composition as a function of temperature is given in Fig. 4 for 4 samples with the different fraction of Ni(0). It has been concluded in the previous researches that the oxidation of the

Fig. 3 XANES spectral change of the perfectly reduced sample during the TPO process from room temperature (blue) to 700 °C (red) under O_2 atmosphere. The dashed line denotes the Ni(0) state before the gas switch from H_2/He to O_2/He.
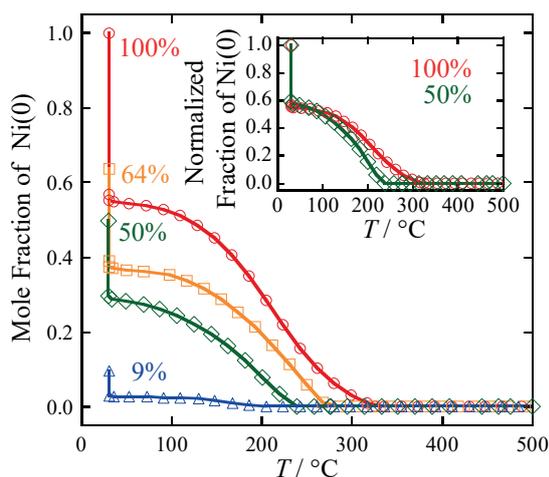
Fig. 4 The fraction change of the Ni(0) state as a function of temperature during the TPO process. The changes of the Ni(0) fraction normalized at room temperature are compared in the inset for two samples with the initial Ni(0) fraction of 100% and 50%.

Ni(0) particle proceeds from the particle surface to the inner core [2,4]. The oxidation of the core part for the larger particle requires the higher temperature, because the volume expansion of the thicker NiO shell is necessary to progress the core oxidation. In this study, although the Ni(0) core size has been changed by varying the fraction of Ni(0), the particle size is the same for all samples. In an inset of Fig. 4, the curves of the Ni(0) composition are compared after the normalization of the Ni(0) fraction at room temperature for two samples with the initial Ni(0) fraction of 100% and 50%. The oxidation temperatures of these two samples are regarded to be consistent within the experimental uncertainty. This study thus supports the previously concluded oxidation mechanism of the Ni(0) particle.

4. Conclusions

The oxidation reaction of the Ni(0) particles with the heterogeneous distribution of the oxidation state of Ni has been investigated in this study. The O_2 exposure caused the surface oxidation of the partially reduced Ni(0) part, and then the Ni(0) core was surrounded by the NiO shell. The precise analysis of the oxidized portion after the O_2 exposure at room temperature clarified the reduction process of the NiO particle, *i.e.*, the reduction of NiO begins at the specific surface site and the reduced region expands toward the particle core by digging into the particle. The Ni(0) composition change observed for the succeeding TPO process supported the oxidation reaction initiated at the particle surface and proceeded to the inner core.

This study has demonstrated the heterogeneous distribution of the oxidation state of Ni in a single particle, and it has been clarified that the size of the Ni(0) core in the NiO particle is possible to be changed by the control of the termination temperature at the pre-reduction procedure. Such the Ni(0) core possesses the covering NiO layer at the particle surface, which can provide the useful ability as the oxidation catalyst.

References

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