Reduction Mechanism of NiO Particle Supported on SiO$_2$

Shunsuke Osaka[1], Yusaku Yamamoto[1], Hirokazu Kitazawa[1], Misaki Katayama[1,2], and Yasuhiro Inada[1]

1) *Department of Applied Chemistry, College of Life Sciences, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu 525-8577, Japan*
2) *The SR Center, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu 525-8577, Japan*

The chemical state conversion of the Ni species supported on SiO$_2$ has been analyzed by *in situ* XAFS measurements. The composition change by the gas switch from H$_2$ to O$_2$ for the partially reduced NiO particles indicates that the metallic Ni(0) species exists at both the particle surface and the inner core. In addition, the analysis on the reduction property suggests that the oxidized Ni species is located at the adjacent place to the metallic Ni(0) species. It is concluded that the metallic Ni(0) and NiO species are heterogeneously distributed in the Ni particle under the reaction condition. The reduction of the NiO particle was initiated at the highly reactive spots and was expanded peripherally. This study achieved to find out the detailed reduction mechanism of the NiO particle supported on SiO$_2$.

1. Introduction

The supported Ni catalysts have the catalytic activity for various reactions, such as the steam and dry reforming reactions of hydrocarbons [1,2] and the methane decomposition reaction [3]. Therefore, the Ni catalyst is expected as the alternative material of noble metal catalysts. The Ni species under the reaction conditions is exposed to reactants and products, and the oxidative and reductive gasses may cause the chemical state conversion of the Ni species. It is thus important to understand the chemical state conversion of the Ni species under the actual reaction conditions in order to improve the catalytic performance and to generate the new catalytic functions.

The X-ray absorption fine structure (XAFS) technique is a powerful tool to characterize the chemical state of supported metal catalysts, because the information of active metal species is available under the actual reaction conditions by *in situ* measurements. The redox properties of the SiO$_2$-supported Ni catalyst have been investigated by the *in situ* XAFS technique [4-6]. The metallic Ni(0) particles were partially oxidized to NiO by the O$_2$ gas exposure at room temperature [4]. The fraction of the oxidized Ni species was increased with decreasing the Ni(0) particle size, and this relationship indicated that the oxidation was proceeded at the particle surface [5]. Moreover, it was revealed that the oxidation temperature of the small Ni(0) particle was lower than that of the large particle. The particle size dependence of the oxidation temperature suggested that the oxidation of metallic Ni(0) species was proceeded from the particle surface to the inner part. The reduction of the NiO particle proceeded at two different temperatures on SiO$_2$. The investigations on the reduction process for a series of different particle sizes revealed that the NiO species located at the interface between the SiO$_2$ support and the NiO particle was stabilized by the formation of the Ni(II)-silicate-like state [6].

These results suggest that the NiO species is spatially localized in the Ni particle during the redox process, that is, the interface NiO species is remaining during the reduction process and the surface NiO species is first generated during the oxidation process. In other words, two different states, NiO and metallic Ni, are simultaneously generated in a supported Ni particle. If the location of those states is possible to be controlled, we will provide the synergetic effect between those species to improve the catalytic performance and to construct a new catalysis system. It is thus necessary and important to understand the formation mechanism of such the mixed chemical states and to clarify their redox properties. The main object of this investigation is to evaluate the detailed mechanisms of the reduction process of the NiO particle supported on SiO$_2$. The reduction process of the NiO particle was terminated before the completion, and the mixed chemical states of the Ni species was quenched by the termination of the reduction process. The O$_2$ exposure at room temperature has been carried out to examine the content of the surface exposed Ni(0) species, and the reduction property of the generated surface NiO species has been studied by *in situ* XAFS measurements during the temperature-programmed reduction (TPR) process.

2. Experimental

The SiO$_2$-supported Ni catalysts were prepared by the impregnation method under the existence of the stoichiometric amount of malonic acid relative to Ni^{2+} in the precursor solution to control the

particle size. The Ni loading was set to be 5 wt%.

The XAFS measurements at the Ni K edge were performed at BL-3 of the SR center (Ritsumeikan Univ.) and at BL-9C and -12C of the Photon Factory (High Energy Accelerator Research Organization). The sample powder was set in a flow-type *in situ* XAFS cell. The SiO_2-supported NiO catalyst was first partially or perfectly reduced under the H_2 atmosphere, and the oxidation process was then conducted by an exposure of the diluted O_2 gas at room temperature. After the O_2 exposure, the flow gas was switched from O_2 to H_2 (10 vol% balanced by He, total flow rate 100 cm^3/min), and the sample was heated from room temperature to 700 ºC with the heating rate of 10 ºC/min. The *in situ* XAFS measurements were carried out during these redox processes.

3. Results and Discussion

The XANES spectral change during the initial reduction process is shown in Fig. 1 for the case of the perfect reduction of NiO. The initial spectrum was identical to that of the reference NiO. The X-ray absorbance at the white line of NiO (8347 eV) was decreased, and the absorption edge was shifted to the lower energy side with the increase in temperature. The absorption edge was finally in agreement with that of Ni foil at 700 °C. The clearly observed isosbestic points indicated the two phase conversion between NiO and metallic Ni(0).

The heating process to reduce the NiO species was stopped at 300 °C and 336 °C to generate the
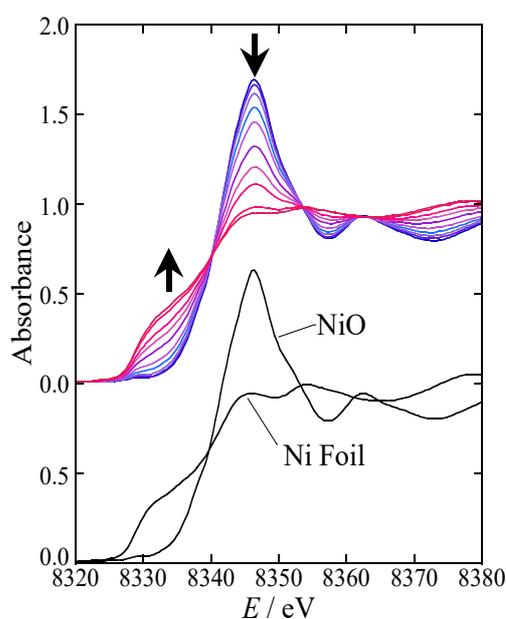
Fig. 1 XANES change during the pretreatment process from room temperature to 700 ºC under H_2 atmosphere.

mixed NiO and Ni(0) states with their different compositions, and the formed chemical-state distribution was quenched by cooling down the temperature. The XANES spectra of such partially reduced catalysts were shown in Fig. 2. The linear combination fitting (LCF) analysis based on the XANES spectrum was performed to determine the composition, and the estimated mole fraction of Ni(0) species was 19% (stopped at 300 °C), 41% (336 °C), and 100% (700 °C).
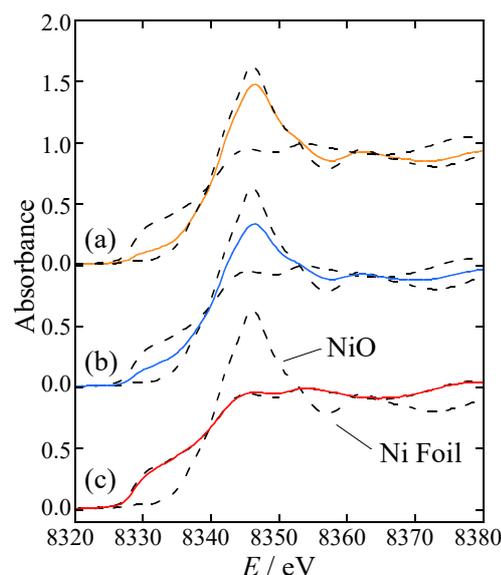
Fig. 2 XANES spectra of SiO_2-supported Ni catalysts with various composition. The quenched temperature during the reduction process was 300 °C (a), 336 °C (b), and 700 °C (c). The reference XANES spectra of Ni foil and NiO are given for comparison (dashed lines).

The XANES change for the O_2 exposure at room temperature is shown in Fig. 3 for the Ni catalysts with the different mixed composition of NiO and Ni(0). The absorbance at the white line was clearly increased and the absorbance at the absorption edge was decreased by the O_2 exposure for all samples. Considering the results of previous study, this spectral change corresponds to the oxidation of metallic Ni(0) located at the particle surface [5,6]. Figure 3 demonstrated that all samples with different Ni(0) composition possess the exposed Ni(0) species at the particle surface. The mole fraction of Ni(0) species determined by the LCF analysis is summarized in Table 1. The surface oxidation of the completely reduced sample indicated that 27% of Ni species located at the particle surface in this sample. However, only 5% of metallic Ni(0) species was oxidized by O_2
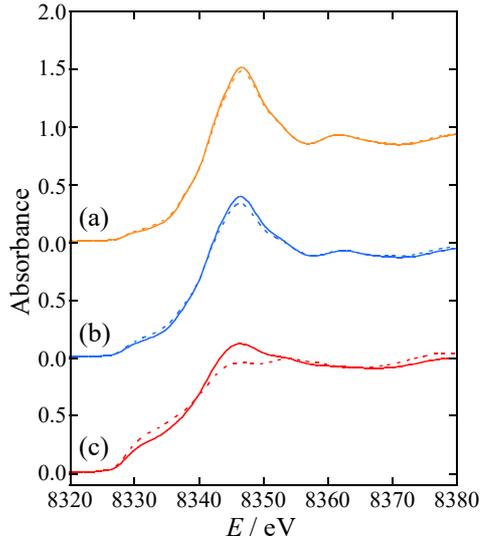
Fig. 3 XANES spectral change of the Ni particle with different proportion of metallic Ni(0) by the O_2 exposure at room temperature. The reduction composition was 19% (a), 41% (b), and 100% (c). The dash and solid lines represent the XANES spectrum before and after the O_2 exposure, respectively.

exposure for the 19%-reduced sample. The fraction of surface oxidation was decreased with decreasing the reduction ratio. It is strongly suggested that the partially formed metallic Ni(0) exists not only at the particle surface but also in the inner part.

Table 1 The mole fraction of metallic Ni(0) species before and after the O_2 exposure.

mole fraction of metallic Ni(0) / %		
under H_2	under O_2	oxidized species ($H_2 - O_2$)
19	14	5
41	31	10
100	73	27

Figure 4 shows the composition change of the Ni(0) species during the TPR process after the O_2 exposure at room temperature. The NiO species existed at the particle surface and on the metallic Ni(0) species was reduced at below 200 °C (Fig. 4(a)), although the reduction of the bulk NiO species proceeded at above 300 °C (Fig. 4(d)). Such the easy reduction at low temperature indicates that the NiO species existed on the metallic Ni(0) species is destabilized for the reduction process because of the lattice mismatch, and thus such the NiO species has the strong property to release the oxide ion, that is, the high oxidizing ability.

For partially reduced samples with the Ni(0)
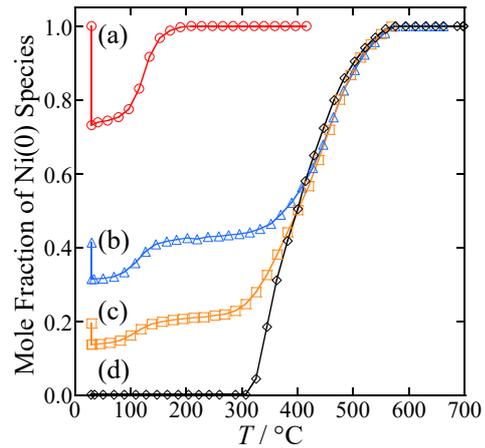
Fig. 4 The mole fraction change of the Ni(0) species as a function of temperature during the TPR process after the O_2 exposure at room temperature. The reduction composition was 100% (a), 41% (b), 19% (c), and no reduction (d).

composition of 19% (Fig. 4(c)) and 41% (Fig. 4(b)), the reduction processes occurred at two different temperature regions (below 200 °C and above 300 °C) after the O_2 exposure. All the surface NiO species generated by the O_2 exposure was reduced ar below 200 °C, and the mole fraction of the metallic Ni(0) at 200 °C was in agreement with that before the surface oxidation. The reduction temperature was the same with that of the surface NiO species existed on the Ni(0) species (Fig. 4(a)). It is indicated that the formed NiO species exists on the metallic Ni(0) species for the partially reduced samples. In addition, the NiO species in the inner part of the particle also existed in the partially reduced samples, and such NiO species was reduced at the temperature above 300 °C, which was in agreement with the reduction temperature of bulk NiO particle (Fig. 4(d)). These results thus lead to the conclusion that the reduction of the NiO particle starts at the specific surface sites, and the reduction is propagated into the inner part of the NiO particle and to the adjacent area around the site. This mechanism reasonably explains that the formed metallic Ni(0) species exists at both the particle surface and the inner part of the particle for the partially reduced samples.

The diagram for the reduction process of the SiO_2-supported NiO particle is schematically illustrated in Fig. 5. The reduction of NiO particle is initiated at the specific surface site and proceeds from the surface to the inside of the particle. At the early phase of the reduction process, not only the metallic Ni(0) species but also the NiO species exists at the particle surface. Then, the reduction of the remaining NiO species is beginning at around

the preferentially reduced site. Therefore, the NiO species formed by the O_2 exposure at room temperature can generate the surface NiO species existed on the inner Ni(0) species, which is reduced at low temperature below 200 °C. The reduction is then propagated into the inner part of the NiO particle and to the adjacent area around the preferentially reduced site. The NiO species stabilized by the SiO_2 support at their interface is remained, and such the stabilized NiO species is finally reduced at above 600 °C [6]. This study has successfully clarified the detailed reduction mechanism of the NiO particle supported on SiO_2.
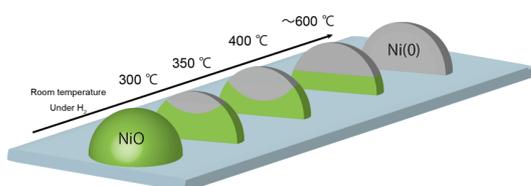
Fig. 5 The reduction mechanism of the NiO particle supported on SiO_2.

4. Conclusions

In the present study, the reduction mechanism of the NiO particle supported on SiO_2 has been revealed by the *in situ* XAFS technique. The analysis on the surface oxidation for the partially reduced NiO particles revealed that there are metallic Ni(0) species at both the particle surface and the inner part at the early stage of the reduction process. Both the NiO and Ni(0) species are simultaneously existed at the particle surface, and such the particle can work as the active site for the reactions, for which the synergetic effect can contribute to facilitate the reaction. The NiO species formed by the O_2 exposure at the particle surface on the Ni(0) species has been easily reduced at low temperature below 200 °C, suggesting that such the NiO species can work as a good active center for the oxidation reaction. In addition, such the partially reduced and the surface oxidized particles possess the stabilized NiO species at the interface with the SiO_2 support. The interface NiO species can work as the anchor to prevent the aggregation of the particle, which is useful to restrain the deactivation due to the decrease in the active surface area. The resulting inhomogeneous distribution of the two different chemical species, NiO and Ni(0), in the Ni particle suggests the possibility to show the high catalytic activity by the combination effects between Ni(0) and NiO. The precise analysis of the reduction mechanism for the NiO particle has achieved by the utilization of *in situ* XAFS technique to the mixed Ni(0) and NiO states formed under the operando conditions.

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