Redox Reactions of Nickel Species Supported on Silica

Shohei Yamashita[1], Misaki Katayama[2], Yasuhiro Inada[2]

1) *Department of Applied Chemistry, College of Science and Engineering, Ritsumeikan, University, 1-1-1 Noji-Higashi, Kusatsu 525*-8577, *Japan*
2) *Department of Applied Chemistry, College of Life Sciences, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu 525*-8577, *Japan*

Abstract

The chemical states of nickel species have been analyzed by means of the X-ray absorption fine structure (XAFS) spectroscopy for the nickel catalysts supported on silicaprepared by impregnation method. The *in-situ* XAFS measurements have been carried out during the temperature-programmed reduction and oxidation processes by varying temperature from 300 K to 873 K under the diluted hydrogen and oxygen atmosphere, respectively. The reversible exchange between NiO and Ni(0) states is observed, and the reduction of NiO is found to proceed at the temperature range from 553 K to 673 K for all samples with different Ni loading. At lower temperature, the surface reduction of NiO particles is not observed under the hydrogen atmosphere, while the exposure of oxygen gas to the metallic Ni(0) particle is found to promote the dispersion of the metallic particle at room temperature.The *in-situ* XAFS analysis reveals that the surface Ni(0) particle is oxidized to form the NiO shell around the Ni(0) core followed by the bulk oxidation. Because the lower Ni loading results in the higher dispersion of the Ni(0) particle, the bulk oxidation proceeds at lower temperature for the sample with lower Ni loading. The surface Ni(0) species is found to be very sensitive to the atmosphere. The surface Ni(0) species is easily oxidized to NiO even at room temperature, while the NiO particle resists to the reduction under the hydrogen atmosphere at the temperature range lower than *ca*. 500 K.

1. Introduction

The supported catalysts play important roles in the modern society. The toxic components ingas emissions from industrial factory areconverted into nontoxic gases by means of the heterogeneous catalyst supporting metal species. All automobiles are equipped the catalyst converter to reduce the toxic components in the exhaust gas. The chemical industry uses metal supported catalysts to generate useful materials for the human society. For such purposes, it is well known that the rare metals, such as palladium, platinum, and rhodium, show high catalytic activity for many chemical processes. The finding and utilization of alternative catalysts using more widely available elements, such as manganese, iron, and nickel, is very important and argent subject for resent society because of the lack of rare and expensive metal elements.

The nickel catalysts supported on silica are used to generate hydrogen by the CO_2reforming and the steam reforming reactions of alkane, and the reactions are also important to solve the energy problems of the modern society[1].The supported nickel catalysts on silica show good performance for the conversion of many chemical processes, but the efficiency and the lifetime are largely dependent on not only the preparation method but also the loading of the active nickel species supported on silica. The speciation of the nickel species in the atomic scale under the reaction conditions is thus necessary to understand the properties of nickel catalysts, because the chemical reactivity is affected by the chemical state of the active nickel species.

It is important for supported catalysts to understand the electronic state and the local structure of the active species. The understanding of reaction mechanisms at the atomic scaleis useful information toreduce side reactions, to achieve higher activity, and to maintain longer lifetime for the target chemical reactions. The X-ray absorption fine structure (XAFS) is the powerful technique for heterogeneous catalysts. The local structural information for a supported metal element is selectively available from that of a large amount of coexisting supporting materials by the analysis of the extended X-ray absorption fine structure (EXAFS). The feature of X-ray absorption near edge structure (XANES) is sensitive to the electronic state of a supported metal element. In addition, since the XAFS spectroscopy is applicable to the *in situ* measurements, the electronic state and the local structure can be analyzed for a supported metal element under the reaction conditions, which is crucial to understand the chemical property of the catalyst.

In this study, the chemical states of nickel species have been analyzed by means of the

XAFS spectroscopy for supported nickel catalysts on silica. The nickel catalysts are exposed under the reductive or the oxidative atmosphere in the catalysis process. As the most simple and basic reaction condition, the speciation of nickel species has been carried out under hydrogen or oxygen gas atmosphere at variable elevated temperature. The available information of the nickel speciation is expected to become the fundamental aspects to understand the catalysis reactivity occurred on the nickel particle under much complex reaction conditions for the actual catalysis systems.

2. Experimental Section

The supported Ni catalysts were prepared by the impregnation method using silica (JRC-SIO-10) distributed by the Catalysis Society of Japan. The powder of silica was suspended in an aqueous solution of $Ni(NO_3)_2 \bullet 6H_2O$, and the mixture was stirred for 1 h at 333 K and was dried at 343 K for 72 h. The obtained powder wascalcined at 873 K in air for 3 h. The loading of supported nickel species was changed to be 5, 7, 10, and 15 wt.%.

The XAFS measurements were carried out at BL-3 of the SR Center ofRitsumeikan University and BL-12C of Photon Factory in High Energy Accelerator Research Organization at the vicinity of the Ni K edge in the transmission mode.The Si(220) and Si(111) double crystal monochromator was used to obtain the monochromatized X-ray at BL-3 and BL-12C, respectively. For the XANES measurements, the X-ray energy was scanned from 8296.7 to 8401.7 eV. A wide energy range from 7826.7 to 9431.7 eV was scanned to obtain the EXAFS spectra.The quick-scanning mode was applied for all measurements. The incident and transmitted X-ray intensity was measured by the ionization chambers flowed by the mixture gas of N_2 and Ar.

Sample powder was packed into a sample holder (i.d. 7 mm), and the holder was put into an *in situ*cell for the XAFS measurements. First, the cell was flowed by the diluted hydrogen gas (10 vol.% balanced by helium, 200 cm^3/min) and was heated to 873 K at 10 K/minas the reduction process. After becoming 873 K, the cell was cooled to room temperatureby keeping thegas flow. The gas was changed to the diluted oxygen (10 vol.% balanced by helium, 200 cm^3/min), and the sample was heated to 873 K at 10 K/min under the oxygen gas flow (temperature-programmed oxidation: TPO). Thereafter, the sample was cooled to room temperature by keeping the oxygen gas flow, and the gas was changed to the diluted hydrogen. The sample was heated again to 873 K at 10 K/min under the hydrogen gas flow (temperature-programmed reduction: TPR). The XAFS measurements were carried out during these procedures with the interval of 2 min.

The samples were analyzed after TPO and TPRfor the characterization of the nickel catalysts by means of the X-ray diffraction (XRD), the transmission electron microscope (TEM), and the BET method.

3. Results and discussion

An example of the XANES spectral change is given in Figure 1 for the TPR process from room temperature to 873 K under diluted hydrogen gas flow for15 wt.% nickel supported on silica. The XANES spectrum at the beginning is perfectly consistent with that of NiO, clearly indicating that the nickel species are quantitatively oxidized at the previous TPO process.The final XANES spectrum of the TPRprocess is almost in accordance with that of nickel foil, suggesting that the treatment of the nickel catalyst at 873 K under the diluted hydrogen gas flow quantitatively reduces the nickel species to the metallic Ni(0) particle. The similar XANES spectral changes were observed for other nickel catalysts with different Ni loading. Because some isosbestic points are clearly observed in Figure 1, the reduction from the Ni(II) to Ni(0) state is apparently proceeded in a single step, suggesting that the hypothetical Ni(I) intermediate state is unstable and thus is not detected by the *in situ* XAFS measurement.

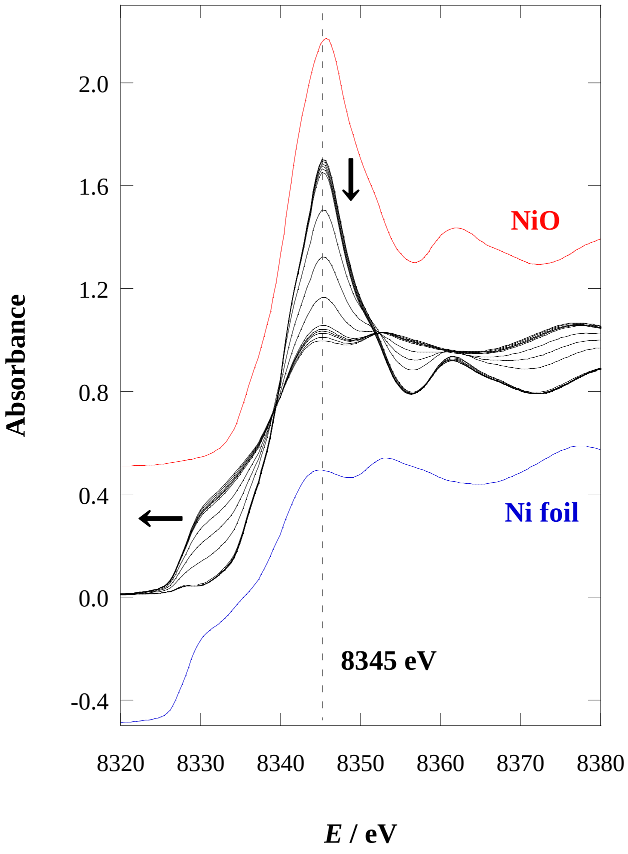

Figure 1. XANES spectral changeduring the TPR process from room temperature to 873 K under diluted hydrogen gas flow for15 wt.% nickel supported on silica.

The reverse changeover from metallic Ni(0) to regenerate the NiO state was observed during the TPO process. The final XANES spectrum of NiO is perfectly in agreement with that at the beginning of TPRshown in Figure 1 for all samples with different Ni loading.The reduction/oxidation reactions between the NiO and Ni(0) particles are reversibly proceeded on silica independent on the Ni loading in the range from 5 to 15 wt.%.

The changes of X-ray absorbance at 8345 eV, which corresponds to the X-ray energy of the white line peak of NiO, are shown in Figure 2 as a function of temperature during the TPO (A) and TPR (B) processes. All results for samples with different Ni loading are compared in Figure 2. The XANES spectra corresponding to the points(a) to (g) in Figure 2 are summarized in Figure 3, in which the coordination numbersobtained by the EXAFS analysis are included for the Ni–O ($N_{\mathrm{Ni–O}}$) and Ni–Ni($N_{\mathrm{Ni–Ni}}$) interactions.

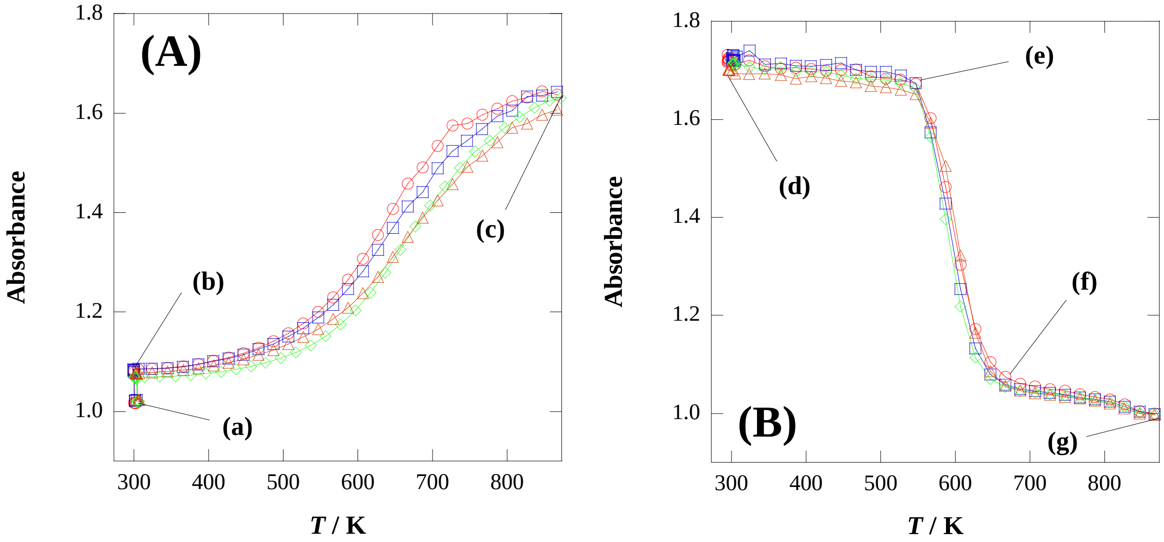

Figure 2. The change of X-ray absorbance at 8345 eVis plotted vs. temperature during the TPO (A) and TPR (B) processes for the Ni supported catalysts with the Ni loading of 5 wt.% (red circles), 7 wt.% (blue squares), 10 wt.% (green diamonds), and 15 wt.% (orange triangles). Some representative conditions are as follows: the hydrogen atmosphere at room temperature just before TPO (a), the oxygen atmosphere at room temperature just after the gas change from hydrogen to oxygen (b), the oxygen atmosphere at 873 K (c), the hydrogen atmosphere at room temperature just after the gas change from oxygen to hydrogen (d), at *ca*. 550 K during the reduction process (e), at *ca*. 670 K during the reduction process (f), and the hydrogen atmosphere at 873 K (g).

At the beginning of the TPO process, the X-ray absorbance is quickly increased as seen in Figure 2(a) and (b). The X-ray absorbance must be increased due to the exchange from hydrogen to oxygen, but the magnitude is too large in considering the absorption coefficient of oxygen and the light path length of the *in situ* cell. According to the EXAFS analyses, the value of $N_{\mathrm{Ni–Ni}}$ is clearly decreased from 11.4 (a) to 10.5 (b) and the Ni–O interaction is not appeared at both points (a) and (b). The intensity of first peak at *ca*. 8345 eV is slightly

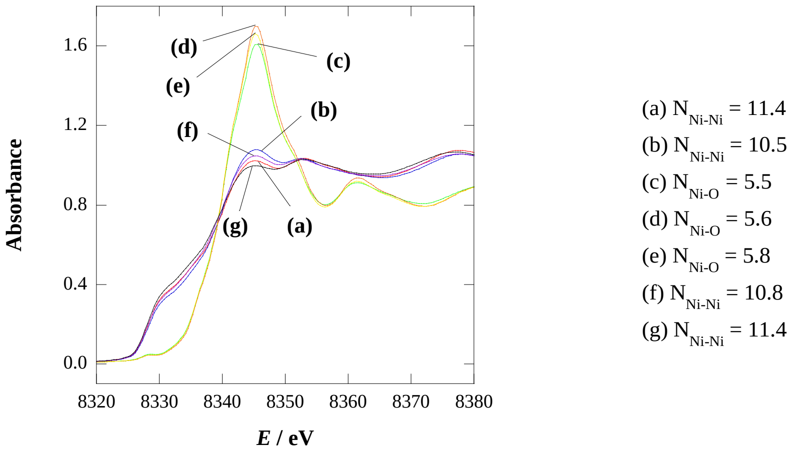

Figure 3. Comparison of XANES spectra during the temperature-programmed oxidation and reduction processes at the points of (a)–(g) in Figure 2. The coordination numbers obtained by the EXAFS analysis are given for the Ni–O ($N_{\text{Ni–O}}$) and Ni–Ni ($N_{\text{Ni–Ni}}$) interactions.

increased from (a) to (b) as seen in Figure 3. Such change is related to the metallic Ni(0) particle size, and the first peak is known to be lower than the second one at *ca*. 8352 eV for the larger particle and the bulk state (see the spectrum of Ni foil given in Figure 1). The quick increase of X-ray absorbance from (a) to (b) is thus concluded to be due to the dispersion of the metallic Ni(0) particle which is promoted by the exposure to the oxygen gas. Very similar but reverse change of the XANES spectra is observed from (f) to (g) during the TPR process. The changes of the XANES spectra and the $N_{\text{Ni–Ni}}$ values indicate that the metallic Ni(0) particle is sintered under the hydrogen atmosphere at high temperature.

As seen in Figure 2A, the X-ray absorbance at 8345 eV is gradually increased until *ca*. 573 K and is drastically increased between 573 K and 723 K during the oxidation process. The two phase change vs. temperature can suggest that the metallic Ni(0) particle have two parts with the different property against the oxidation, *i.e.*, the surface and the inner part of the particle. The surface Ni(0) species isreadily oxidized and the surface part is first changed to NiO until *ca*. 573 K. The surface oxidation at mild temperature lower than *ca*. 573 K thus produces the core-shell particle with the Ni(0) core and the NiO shell. The treatment under higher temperature promotes the oxidation of the Ni(0)-core part, which is necessary to accompany the diffusion of oxygen atoms into the inner part of the particle.The oxidation extent is found to be dependent on the Ni loading.The X-ray absorbance at same temperature is larger for the sample with lower Ni loading, indicating that the larger amount of the nickel species is oxidized when the Ni loading is smaller.This is considered to be caused by the higher dispersion of the Ni(0) particle with smaller diameter at the lower Ni loading.The smaller Ni(0) particle leads to the larger ratio of surface species, and the XANES spectra thus becomes closer to the oxidized form at lower temperature. In addition, it is found that the temperature of the bulk oxidation shifts to higher for the sample with higher Ni loading. This seems to be due to the larger endothermic enthalpy required for the surface oxygen diffusion into the inner part in the case of the larger particle. The final XANES spectra of the TPO process are almost the same except for that of the highest Ni loading, for which the oxidation is not quantitatively completed.

The particle size of the nickel species has been clarified by other characterization techniques, such as XRD and TEM. The larger particle has been observed for the sample with higher Ni loading.It is thus concluded that the Ni loading affects the size of particle.This result is in agreement with the previous reports [2-6]. This study further reveals that the particle size of the Ni(0) species affects to the oxidation tendency and that the smaller particle formed in the sample with the lower Ni loading readily oxidized at lower temperature because of the easy oxygen diffusion from the surface into the inner part.

For the TPR process (see Figure 2B), the X-ray absorbance at 8345 eV is almost unchanged until *ca*. 553 K and is drastically decreased between 553 K and 673 K for all samples with different Ni loading. The XANES spectral change reveals that the reduction of the metallic Ni(0) particle proceeds in the temperature range between 553 K and 673 K.The surface reduction of NiO particle and the inter reduction are thus considered to occur simultaneouslyin that temperature range without any correlations to the Ni loading. After the reduction reaction is almost completed at *ca*. 673 K, the X-ray absorbance at 8345 eV is further slightly decreased with increasing the temperature (see Figure 2(f) and (g)). The XANES spectral change at this step is very similar to the spectral difference between the Ni(0) nanoparticle and the bulk metal (*vide supra*). The treatment of the Ni(0) particle under the hydrogen atmosphere causes the sintering of the Ni(0) particle at temperature over *ca*. 700 K.

4. Conclusion

The chemical states of nickel species have been analyzed by means of the*in-situ* XAFS spectroscopy for the supported nickel catalysts with some different loadingsprepared by impregnation method on silica. The reversible exchange between the NiO and Ni(0) particles is clearly observed by changing the conditions between the oxygen and hydrogen atmosphere.It is found that the exposure of oxygen gas to the metallic Ni(0) particle promotes the dispersion of the metallic nanoparticle at room temperature. The oxidation of dispersed

Ni(0) particle shows the two phase change during the TPO process, *i.e.*, the first surface oxidation to form the NiO shell around the Ni(0) core and the succeeding bulk oxidation which is accompanied by the diffusion of oxygen atoms into the inner part of the particle.Because the lower Ni loading results in the higher dispersion of the Ni(0) particle, the extent of the oxidized species is higher and the bulk oxidation proceeds at lower temperature for the sample with lower Ni loading. In contrast, the NiO particle is simultaneously reduced at the temperature range from 553 K to 673 K, and the surface reduction is not observed at lower temperature range under the hydrogen atmosphere.The treatment of the Ni(0) particle at temperature over *ca*. 700 K causes the sintering of the Ni(0) particle.The *in situ* XAFS analyses for both the TPO and TPR processes has clarified that the surface Ni species of the supported Ni(0) particle on silica is very sensitive to the atmosphere. The exposure to the oxidative gas can convert the surface Ni(0) species to NiO even at the lower temperature range. On the other hand, the NiO particle on silica can resist to the reduction under the hydrogen atmosphere at the temperature range lower than *ca*. 500 K.

Acknowledgment

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