Reduction Kinetics of Nickel Species Supported on Silica

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Abstract. The reaction mechanism of reduction processes of NiO supported on silica has been clarified by means of the time-resolved dispersive XAFS (DXAFS) technique. The reduction of NiO shows two-phase changes. The first reaction corresponds to the reduction of NiO to the metallic Ni particle, and the sintering of the formed Ni particles occurs in the second step. The reduction process is composed of the surface reduction of the NiO particle and the successive oxygen diffusion from the particle core to the surface. The first-order kinetics suggests that the latter is the rate-determining step. The conditional rate constants indicate that the diffusion of oxygen atoms is relatively faster for the lower Ni loading.

1. Introduction
The nickel catalysts supported on silica are used to generate hydrogen by the CO₂ and steam reforming reactions of alkane, and the reactions are important to solve energy problems of modern society [1]. But the efficiency and lifetime are largely dependent on not only the preparation method but also the loading of active Ni species. In this study, the electronic state and local structure of Ni species supported on silica have been studied by varying the loading of Ni. The Ni species have been characterized by in situ XAFS experiments, and the kinetic studies of the reduction of NiO have been carried out by the time-resolved dispersive XAFS (DXAFS) technique.

2. Experimental
The supported Ni catalysts were prepared by the impregnation method using SiO₂ distributed by the Catalysis Society of Japan (JRC-SIO-10). The loading of Ni was changed in the range of 5–20 wt.%. The DXAFS measurements were carried out at NW2A station of PF-AR (KEK, Japan) [2]. Polychromatic X-rays were obtained with a Si(111) bent crystal (Bragg type) and were detected by a linear photodiode array detector equipped with a scintillation (CsI:Tl). Sample powder was placed in an in situ cell for the DXAFS measurements. The H₂ gas was rapidly introduced into the evacuated cell at 873 K to follow the reduction process of Ni species. DXAFS spectra were recorded every 30 ms.

The in situ XAFS measurements were performed at BL-12C station of PF (KEK, Japan). The Si(111) double-crystal monochromator was detuned to remove higher order harmonics. The quick-scanning mode was applied for all measurements. Sample powder was first treated in the in situ cell by the diluted H₂ gas flow at 873 K, and was cooled to room temperature by keeping the gas flow. The gas was changed to the diluted O₂ (10 vol.% balanced by He, 200 cm³/min), and the sample was heated to 873 K at 10 K/min (temperature-programmed oxidation: TPO). Thereafter, the gas was changed to the diluted H₂, and the sample was heated again to 873 K at 10 K/min (temperature-
programmed reduction: TPR). The quick-XAFS measurements were carried out during these processes with the interval of 2 min.

3. Results and discussion
An example of the XANES spectral change is given in Figure 1 for the TPR process for Ni/SiO\(_2\) with the Ni loading of 15 wt.%. The XANES spectrum at the beginning is consistent with that of NiO, clearly indicating that the Ni species are quantitatively oxidized at the previous TPO process. The final XANES spectrum is almost in accordance with that of Ni foil, suggesting that the treatment of the Ni catalyst at 873 K under H\(_2\) quantitatively reduces NiO to the metallic Ni(0) particle. The similar XANES spectral changes were observed for other samples with different Ni loadings.

![Figure 1](image1.png)

**Figure 1.** XANES spectral change during the TPR process from room temperature to 873 K under diluted H\(_2\) gas flow for Ni/SiO\(_2\) with the Ni loading of 15 wt.%. The X-ray absorbance changes at 8345 eV, which corresponds to the white line peak of NiO, are shown in Figure 2 as a function of temperature during the TPR process. The X-ray absorbance is almost unchanged until ca. 553 K and is drastically decreased between 553 K and 673 K for all samples. The XANES spectral change reveals that the reduction of the metallic Ni(0) particle proceeds at the temperature range of 553–673 K. The surface reduction of the NiO particle and the progress into the core of the particle are thus considered to occur in that temperature range without any correlations to the Ni loading. This finding is supported by the almost constant \(N_{\text{Ni:Ni}}\) values determined by the

![Figure 2](image2.png)

**Figure 2.** The changes of X-ray absorbance (left panel) at 8345 eV (broken line in Figure 1) are plotted vs. temperature during the TPR processes for the supported Ni catalysts with the Ni loading of 5 wt.% (circles), 7 wt.% (squares), 10 wt.% (diamonds), and 15 wt.% (triangles) and comparison of XANES spectra (right panel) of 15 wt.% Ni/SiO\(_2\) at the points of (a)–(d).
curve-fitting procedure of the EXAFS data (see Table 1). After the reduction is almost completed at ca. 673 K, the X-ray absorbance is further decreased with increasing the temperature (see Figure 2(c) and (d)). The spectral change at this step is very similar to the corresponding difference between the Ni(0) nanoparticle and the bulk metal. The treatment of Ni(0) particles under the H\textsubscript{2} atmosphere causes the sintering of Ni(0) particles at temperature over ca. 700 K.

Table 1. Structure parameters of reduced Ni species on SiO\textsubscript{2}.

| Sample           | T / K | Interaction | N   | R / pm | σ\textsuperscript{2} / 10\textsuperscript{-5}nm\textsuperscript{2} |
|------------------|-------|-------------|-----|--------|---------------------|
| Ni foil          |       | Ni-Ni       | 12  | 248±1  | 6.2±0.2             |
| 5 wt.% Ni/SiO\textsubscript{2} | 670   | Ni-Ni       | 10.9±1.2 | 250±2   | 12.2±1.4           |
|                  | 873   | Ni-Ni       | 11.8±0.6 | 250±1   | 15.2±0.5           |
| 7 wt.% Ni/SiO\textsubscript{2} | 670   | Ni-Ni       | 11.4±1.2 | 250±1   | 12.5±0.8           |
|                  | 873   | Ni-Ni       | 11.5±0.6 | 250±1   | 14.8±0.5           |
| 10 wt.% Ni/SiO\textsubscript{2} | 670   | Ni-Ni       | 11.2±1.2 | 250±1   | 12.2±0.9           |
|                  | 873   | Ni-Ni       | 11.2±0.5 | 250±1   | 14.5±0.4           |
| 15 wt.% Ni/SiO\textsubscript{2} | 670   | Ni-Ni       | 10.0±2.7 | 249±1   | 11.3±2.2           |
|                  | 873   | Ni-Ni       | 10.9±0.7 | 250±1   | 14.4±0.6           |

The X-ray absorbance changes at 8345 eV obtained by the DXAFS measurements are shown in Figure 3 as a function of time during the reduction process. The reduction of NiO shows two-phase changes. The first reaction, which is completed within ca. 5 s, corresponds to the reduction of NiO to the metallic Ni(0) particle, supported by the XANES spectral change. The sintering of the formed Ni(0) particles proceeds at the slow second step in the order of minutes. These results are in agreement with the observations of in situ XAFS experiments (vide supra). The X-ray absorbance change during the reduction of NiO is represented by a single exponential function. Because the reduction process must be composed of the surface reduction of NiO particles to generate surface Ni(0) state and the successive oxygen diffusion from the NiO core to the surface, the first-order kinetics on Ni suggests that the latter process is a rate-determining step.

![Figure 3](image-url)

Figure 3. The change of X-ray absorbance at 8345 eV is plotted vs. time during reduction processes at 873 K for 5 wt.% NiO/SiO\textsubscript{2} in A. The H\textsubscript{2} pressure was 2.6 kPa (a), 4.1 kPa (b), and 9.4 kPa (c). In B, the conditional first-order rate constants for the fast reduction process are plotted against H\textsubscript{2} pressure for 5 wt.% (a), 10 wt.% (b), and 15 wt.% (c) NiO/SiO\textsubscript{2}.

As schematically shown in Figure 4, the first reduction process is initiated by an adsorption of H\textsubscript{2}, and the adsorption equilibrium constant is represented by K\textsubscript{A}. The surface NiO species (NiO*) is reduced by an adsorbed H\textsubscript{2} with the rate constant of k\textsubscript{1} to form the surface Ni(0) species (Ni*), which is reversely oxidized with the rate constant of k\textsuperscript{-1}. The internal O atoms are diffused with the rate...
constant of $k_2$ from the NiO core to the surface Ni* species, leading to the regeneration of NiO*. The change of the number of Ni* ($N_{Ni^*}$) is then given in Eq. (1),

$$\frac{dN_{Ni^*}}{dt} = k_2 \theta H_2 N_{NiO^*} - k_{-1} N_{Ni^*} - k_2 N_{Ni^*} N_{NiO}$$

where $\theta_{H2}$ and $N_X$ denotes the surface coverage of H$_2$ and the number of species X, respectively. Assuming the steady state to the Ni* species, the $N_{Ni^*}$ term is represented by Eq. (2) under the approximation that the $k_2$ step is rate determining,

$$N_{Ni^*} = \frac{k_1 \theta H_2 N^S}{1+K_1 \theta H_2}$$

where $K_1$ represents the equilibrium constant of the surface redox reaction ($K_1 = k_1/k_{-1}$) and $N^S$ denotes the total number of surface nickel species (NiO* and Ni*). The conditional first-order rate constant ($k_{obs}$) is thus derived as Eq. (3) by assuming that $N^S$ is constant vs. time.

$$-\frac{dN_{NiO}}{dt} = \frac{k_2 k_1 \theta H_2 N^S}{1+K_1 \theta H_2} N_{NiO} = k_{obs} N_{NiO}$$

The hydrogen pressure dependence of $k_{obs}$ is expected to show a saturating behavior according to Eq. (3). The limiting value of $k_{obs}$ under high H$_2$ pressure is then approximated to Eq. (4),

$$k_{obs} \approx k_2 K_1 N^S$$

where the $K_1$ value is treated to be much smaller than 1, since the reduction of NiO is observed with clear isosbestic points. The $k_{obs}$ values are plotted vs. $P_{H2}$ in Figure 3B, in which the saturating dependence is clearly demonstrated. It has clarified that the limiting $k_{obs}$ value under the low Ni loading is larger than that under the high Ni loading, indicating that the migration of internal O atoms is relatively faster for small Ni(0) particles. This mechanism has been clarified for the first time by applying the kinetic analysis to the solid-phase redox reactions for the supported Ni species.

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References
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