

# Surface Oxidation Mechanism of Ni(0) Particle Supported on Silica

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## Abstract

The chemical state of nickel species was analyzed by means of the X-ray absorption fine structure (XAFS) spectroscopy for Ni catalysts supported on SiO<sub>2</sub> prepared by the impregnation method. The *in-situ* XAFS and DXAFS measurements were carried out on the surface oxidation process for metallic Ni(0) particles at room temperature under oxygen atmosphere. The Ni(0) state was generated by the *in-situ* reduction at 873 K as a pretreatment, and was partially oxidized by a rapid introduction of O<sub>2</sub> gas within *ca.* 1 s at room temperature. The kinetic analyses revealed the surface oxidation mechanism of the Ni(0) particle. The rate constants depended on the injected O<sub>2</sub> gas pressure, and the pressure dependence showed a saturated curve. The pressure dependence indicates that the dissociative adsorption of an O<sub>2</sub> molecule exists as a pre-equilibrium of the rate-determining oxidation of the surface Ni(0) atom. Because there is a great energy barrier for the oxygen migration into the particle core at room temperature, the Ni(0) core and NiO shell particles are generated under the oxygen atmosphere.

## 1. Introduction

Chemical reactions of heterogeneous catalysis systems proceed on a particle surface of active species. The supported Ni catalysts show high activity for hydrogen and syngas formations by the reforming reaction of methane [1], and are also used to control the H<sub>2</sub>/CO ratio in the formed syngas by the reforming reaction of carbon dioxide [2]. The Ni catalyst thus attracts a great interest as an alternative material of the rare elements with high activity.

The short lifetime of the supported Ni catalyst is a major problem to be solved for the actual utilization in the chemical industry. The deactivation is mainly due to the sintering of the Ni particle, the formation of carbon, and the surface modification by the environment gas. The sintering of the supported Ni particle is one of serious problems for the steam reforming reaction of methane. It is reported that the catalysis activity is significantly depend on the Ni particle size [3]. The distribution of the Ni particle was easily broadened by a thermal treatment over 673 K [4]. Various mesoporous supporting materials were applied to keep the Ni particle size [5], and the sol-gel method was used to prepare the Ni catalyst to prevent the sintering of the Ni species [6]. The formation of carbon on the Ni catalyst is also a problem because the adsorption of reaction gas molecules is inhibited. It has been reported that the use of silica as the supporting material is advantage to reduce the formation of carbon in comparison to alumina [7], and the addition of CeO<sub>2</sub> also contribute to the reduction of carbon to keep the high catalytic activity [8]. The remaining problem is the surface chemical conversion of the supported Ni species caused by the gas atmosphere. The surface of metallic Ni particles is easily oxidized and is covered with NiO [9,10]. This causes the marked reduction of the active surface area as the metallic Ni catalyst. The formation of stable and inactive Ni compound, such as Ni<sub>3</sub>C, is known to degrade the steam reforming performance [11].

The speciation of the Ni species under the reaction conditions is thus necessary to understand the properties of the Ni catalyst, because the chemical reactivity is affected by the chemical state of the active Ni species. It is important for supported catalysts to understand the electronic state and the local structure of the active species. An evaluation of the reaction mechanism is essential information to reduce 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 the speciation of heterogeneous catalysts. The local structure for a supported metal element is selectively available even in 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, because the XAFS technique is applicable to the *in-situ* measurements, the electronic state and the local structure can be analyzed for a supported metal species under the reaction conditions, which is crucial to understand the chemical property of the catalyst. Furthermore, an application of the time-resolved dispersive XAFS (DXAFS) technique with the time resolution of ms is very useful to evaluate the reaction mechanism by the kinetic analysis.

In this study, the chemical states of the Ni species have been investigated by means of *in-situ* XAFS and DXAFS techniques for supported Ni catalysts on SiO<sub>2</sub>. The Ni catalysts were exposed under an O<sub>2</sub> atmosphere at room temperature, and the speciation of the Ni species was carried out to clarify the surface oxidation process of the Ni(0) particle. The kinetic analysis for the surface oxidation process was performed using the time-resolved DXAFS technique. The mechanistic information about the surface oxidation is fundamental to understand the chemical conversion process from Ni(0) to NiO for the supported Ni catalyst. In the previous work [12], we have investigated the bulk oxidation mechanism for the supported Ni(0) particle, and have clarified that the first-order kinetics on the Ni species indicates the fast surface oxidation followed by the rate-determining oxygen migration in the particle core. The present study focuses on the early stage of the bulk oxidation process, and will reveal the detail mechanism of the surface oxidation process, which initiates the deactivation of the metallic Ni catalyst.

## 2. Experimental

The supported Ni catalyst was prepared by the impregnation method using SiO<sub>2</sub> (JRC-SIO-10) distributed by the Catalysis Society of Japan. The powder of SiO<sub>2</sub> 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 333 K and was dried at 343 K for 72 h. The obtained powder was calcined at 873 K in air for 3 h. The loading of supported Ni species was set to be 10 wt%.

The *in-situ* XAFS measurements were carried out at BL-3 of the SR Center of Ritsumeikan University and BL-12C of Photon Factory in High Energy Accelerator Research Organization (KEK) at the vicinity of the Ni K edge in the transmission mode. The Si(220) and Si(111) double crystal monochromator was used at BL-3 and BL-12C, respectively. The X-ray energy was scanned from 8297 to 8402 eV for the XANES measurements. A wide energy range from 7827 to 9432 eV was covered to obtain the EXAFS spectrum. 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<sub>2</sub> and Ar. The mixing ratio was adjusted to become the suitable transmittance.

Sample powder was packed into a cylindrical sample holder (i.d. 7 mm), and the holder was put into an *in-situ* XAFS cell. First, the calcined Ni catalyst was heated until 873 K at 10 K/min under the flow of dilute H<sub>2</sub> gas (10 vol.% balanced by He, 200 cm<sup>3</sup>/min) to complete the reduction of the supported Ni species. After becoming 873 K, the cell was cooled down to room temperature by keeping the H<sub>2</sub> gas flow, and the flowing gas was switched to dilute O<sub>2</sub> gas (10 vol.% balanced by He, 200 cm<sup>3</sup>/min). The repetition of XAFS measurements was started before the gas change.

The DXAFS measurements were performed at NW2A of PF-AR (KEK). A Bragg-type Si(111) curved crystal with the bending radius of 3 m was used as a polychromator. The X-ray energy was calibrated by measuring a XAFS spectrum of Ni foil. Sample holder was located in the DXAFS cell, and the atmosphere gas in the cell was evacuated. The cell was heated to 873 K, and a H<sub>2</sub> gas was injected to reduce completely the supported Ni species. The cell was cooled down to room temperature by keeping the H<sub>2</sub> gas atmosphere. The cell was evacuated again, and the DXAFS spectra were measured every 30 ms at room temperature after a rapid injection of O<sub>2</sub> gas to monitor the dynamic process of the surface oxidation. When the injected O<sub>2</sub> gas pressure was changed, the reduction procedure by H<sub>2</sub> was repeated at 873 K before the DXAFS measurements at room temperature.

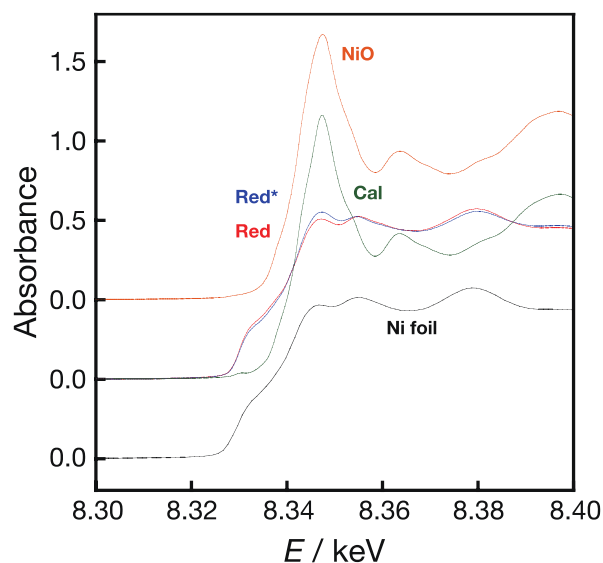
The air-exposed reduced samples were also characterized by the X-ray diffraction (XRD) and the X-ray photoelectron spectroscopy (XPS). The particle size was estimated by means of the transmission electron microscope (TEM).

### **3. Results and discussion**

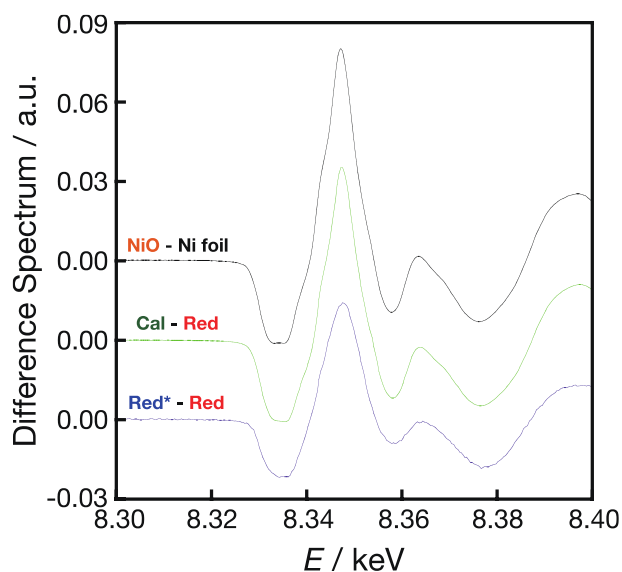
#### **3.1. Chemical state of supported Ni species on SiO<sub>2</sub>**

The normalized XANES spectra were shown in Fig. 1. The normalization was carried out based on the smooth K shell absorption estimated in the EXAFS region. The calcined Ni species depicted by a green line was perfectly consistent with that of reference NiO. The formation of NiO after the calcination was confirmed by the XRD measurement. The red line in Fig. 1 shows the XANES spectrum measured at room temperature after the reduction treatment by H<sub>2</sub>, and is in accordance with that of Ni foil, indicating the quantitative reduction of supported NiO. The gas switch from H<sub>2</sub> to O<sub>2</sub> changes the XANES spectrum slightly as shown by a blue line in Fig. 1. The X-ray

absorbance at the white line peak of NiO was slightly increased. The characteristics of the spectral difference are very similar to that between the NiO and Ni(0) species supported on SiO<sub>2</sub> reported in the previous study [12], in which the bulk redox reactions have been investigated using the *in-situ* XAFS technique. The slight change of the XANES spectrum is therefore assigned to the partial oxidation caused by the contact with O<sub>2</sub> at room temperature. Although the corresponding change was not observed by the XRD measurement, the partial formation of NiO was confirmed by the XPS spectrum, in which both signals assigned to Ni(II) and Ni(0) were observed. Because it is expected that the probe depth of the XPS technique is *ca.* 10 nm, both the surface NiO and its inner Ni(0) atoms have been detected. The difference XANES spectra are compared in Fig. 2. The difference spectrum (Red\*-Red in Fig. 2) at the slight XANES change after the switch to O<sub>2</sub> atmosphere is perfectly in agreement with that between NiO and Ni foil. The spectral agreement supports the partial oxidation of the Ni(0) particle.



**Fig. 1** XANES spectrum of the supported Ni catalyst after the calcination (green), the reduction by H<sub>2</sub> (red), and the switch of the atmosphere gas to O<sub>2</sub> (blue). All spectra were measured at room temperature. The reference spectra of bulk NiO and Ni foil are included.



**Fig. 2** The difference XANES spectra for various Ni species. The denotations are the same with those in Figure 1. The spectra of “NiO–Ni foil” and “Cal–Red” were divided by 10.

The Fourier transform function of the EXAFS oscillation given in Fig. 3 clearly shows the formation of NiO after the calcination and the quantitative reduction by the H<sub>2</sub> treatment. The slightly weak intensity of the interaction peaks suggests the dispersion of the Ni species on SiO<sub>2</sub>. The Fourier transformation (blue in Fig. 3) of the partially oxidized Ni catalyst formed after the introduction of O<sub>2</sub> gas is almost consistent with that of the reduced state except for the slight decrease of the Ni–Ni interaction peak intensity. This minor difference indicates the partial oxidation of the Ni(0) species. Although the existence of NiO is demonstrated by the difference XANES (Fig. 2) and the XPS spectra, the nearest neighboring Ni–O interaction and the longer Ni–Ni and Ni–O interactions are not observed in the Fourier transform function. The preliminary simulations of the Fourier transform function for the mixed samples of NiO and Ni(0) with a series of the mixing ratio demonstrate that the interaction peaks assigned to NiO are appeared in the case of the composition of NiO greater than 20 %. The simulation also estimates the composition of NiO as *ca.* 5 % on the basis of the reduced intensity for the Ni–Ni interaction of the Ni(0) species. The estimated composition was almost in agreement with that calculated by a linear combination fitting (LCF) analysis of the XANES spectrum.

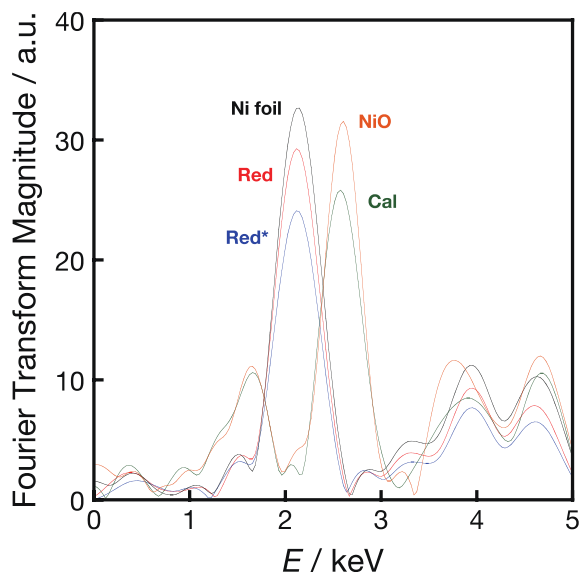


Fig. 3 Fourier transform functions for various Ni species. The denotations are the same with those in Figure 1. The reference data of bulk NiO and Ni foil are included.

### 3.2. Particle size of supported Ni species on SiO<sub>2</sub>

The size of the supported Ni particles in the reduced sample was estimated by TEM, and the distribution histogram of the particle size was shown in Fig. 4 together with a typical TEM image. It is known that the particle size depends on the preparation method and that a wide variation of the particle size is frequently appeared for the conventional impregnation method. The histogram in Fig. 4 clearly shows that the

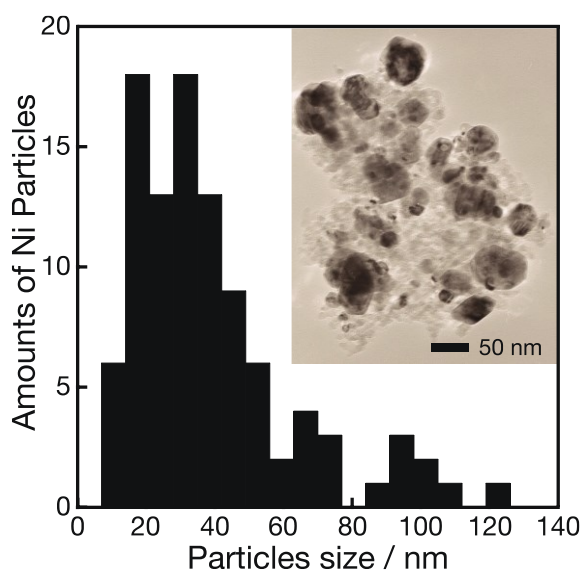
diameter of the Ni(0) particle distributes in the range from 6 to 130 nm with the average value of 38 nm.

When the supported Ni(0) particle is exposed to the O<sub>2</sub> gas atmosphere, it is reasonable to consider that the particle surface is first oxidized by the direct contact with the O<sub>2</sub> molecule. According to the NiO composition of 5 % estimated by the LCF analysis of the XANES spectrum, the shell depth of *ca.* 3 Å is calculated for NiO in the case of the average particle size of 38 nm, *i.e.*, the O<sub>2</sub> exposure leads the outer-layer oxidation of the

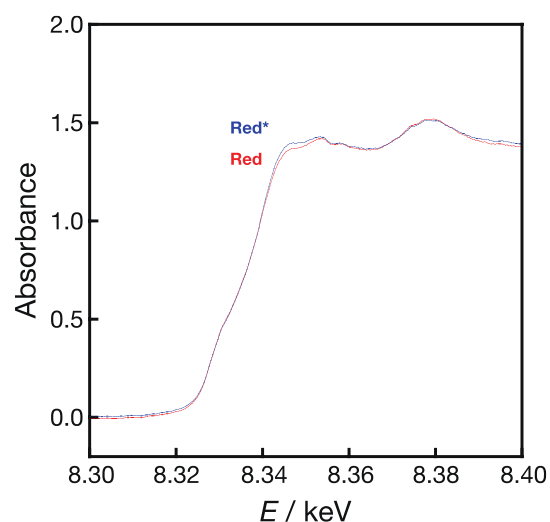
Ni(0) particle with the depth of *ca.* 3 Å at room temperature. The estimated layer depth means that only the surface Ni(0) species experiences the oxidation, because the interatomic Ni–Ni distance of the metallic Ni is 2.48 Å. This result indicates that the surface of any Ni(0) catalysts is oxidized after their exposure to air and that the core Ni(0) atoms are covered with the NiO surface layer. Our previous study has revealed that the surface O atoms bound to the Ni(II) ion migrates into the core region at higher temperatures by accompanying the electron transfer between the Ni(II) and Ni(0) atoms, and that the quantitative oxidation is achieved at higher than 873 K under the O<sub>2</sub> atmosphere.

### 3.3. Kinetic analysis of surface oxidation process

Figure 5 shows an example of the XANES



**Fig. 4** The particle size distribution of the supported Ni species for the reduced sample. A typical TEM image is inserted.

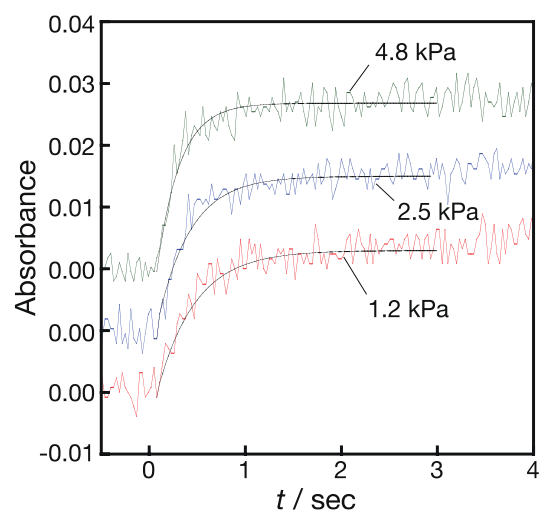


**Fig. 5** XANES spectrum before (red) and after (blue) a rapid injection of O<sub>2</sub> (4.8 kPa) measured by the DXAFS technique at room temperature. The spectrum was measured with the acquisition time of 30 ms.

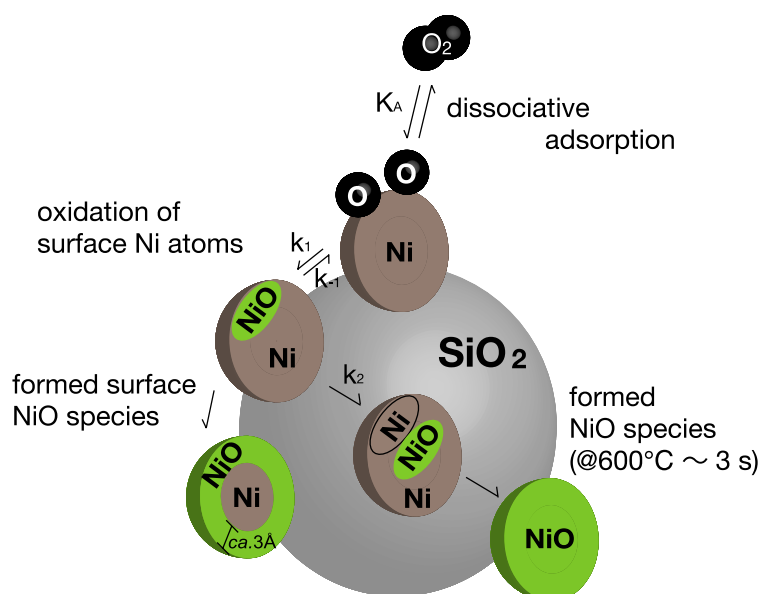
spectral change of the surface oxidation process measured by the DXAFS technique at room temperature. The characteristics of the observed change are almost consistent with those shown in Fig. 1, indicating that the dynamic process of the surface oxidation of the supported Ni(0) particle is monitored with the time-resolution of 30 ms.

The X-ray absorbance changes at 8.347 keV, which corresponds to the white line peak of NiO, are given in Fig. 6 as a function of time. The absorbance was increased after the rapid injection of O<sub>2</sub> and the change was completed within *ca.* 1 s. The observed change for the surface oxidation process was well reproduced by a single-exponential function as seen in Fig. 6. The conditional first-order rate constants ( $k_{\text{obs}}$ ) were determined by the optimization of a single-exponential function.

As schematically shown in Fig. 7, it is considered that the surface oxidation process is initiated by the dissociative adsorption equilibrium of a O<sub>2</sub> molecule on the surface Ni(0) atom. The equilibrium constant is represented by  $K_A$ . The surface Ni(0) atom with the



**Fig. 6** The X-ray absorbance at 8.347 keV plotted versus time during the surface oxidation process at room temperature under three different O<sub>2</sub> pressures. The solid line is the fitted single-exponential function depicted using the optimized kinetic parameters.



**Fig. 7** The proposed surface oxidation mechanisms of SiO<sub>2</sub>-supported Ni(0) particle under O<sub>2</sub> gas atmosphere. The bulk oxidation process ( $k_2$  and its following step) to convert Ni(0) to NiO is included.



adsorbed O atom is oxidized with the rate constant of  $k_1$  to form the surface NiO species, and its reverse reaction is described by the rate constant of  $k_{-1}$ . The quantitative progress of the surface oxidation permits to neglect the  $k_{-1}$  step under the present conditions. Because the oxidation process is regarded to be exothermic, the surface oxidation step tends to be interrupted at higher temperature. The previous study about the bulk oxidation has concluded that the surface oxidation step is the fast and unfavorable pre-equilibrium of the rate-determining  $k_2$  step at 873 K [12], and it is not contradicted to the quantitative progress observed in this study at room temperature.

The reaction scheme given in Fig. 7 permits us to lead the following derivation to describe the observed first-order rate constant of the surface oxidation process. The formation rate of the surface NiO species ( $N_{\text{NiO}^*}$ ) is given by equation (1),

$$\frac{dN_{\text{NiO}^*}}{dt} = k_1 N_{\text{Ni}^* \cdot \text{O}^*} \quad (1)$$

where  $N_{\text{NiO}^*}$  is the number of product and  $N_{\text{Ni}^* \cdot \text{O}^*}$  denotes the number of surface Ni(0) atom with the dissociatively adsorbed oxygen. If the oxygen coverage of the Ni particle surface is expressed as  $\theta$ , the  $N_{\text{Ni}^* \cdot \text{O}^*}$  term is represented by equation (2), in which  $N_{\text{Ni}^*}$  represents the number of surface Ni(0) atom without the adsorbed oxygen.

$$N_{\text{Ni}^* \cdot \text{O}^*} = \frac{\theta}{1-\theta} N_{\text{Ni}^*} \quad (2)$$

If the total number of Ni atoms at the particle surface is written as  $N$  (equation (3)), equation (1) is modified to equation (4).

$$N = N_{\text{Ni}^* \cdot \text{O}^*} + N_{\text{Ni}^*} + N_{\text{NiO}^*} \quad (3)$$

$$\frac{dN_{\text{NiO}^*}}{dt} = k_1 \theta (N - N_{\text{NiO}^*}) \quad (4)$$

By solving the differential equation (4), the  $N_{\text{NiO}^*}$  term is finally expressed by equation (5) as a function of time.

$$N_{\text{NiO}^*} = N \{1 - \exp(-k_1 \theta t)\} \quad (5)$$

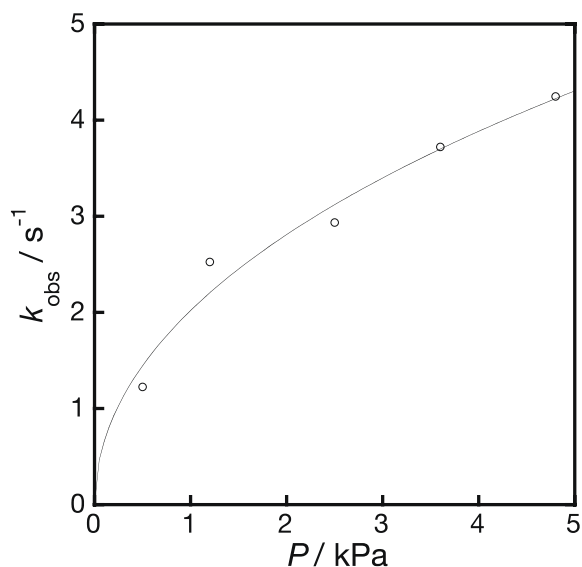
This function is in agreement with the first-order behavior shown in Fig. 6, and thus the  $k_{\text{obs}}$  value shows the  $\text{O}_2$  pressure ( $P$ ) dependence as equation (6) when the molecular oxygen dissociatively adsorbs on the Ni(0) surface.

$$k_{\text{obs}} = k_1 \theta = \frac{k_1 \sqrt{K_A P}}{1 + \sqrt{K_A P}} \quad (6)$$

The determined  $k_{\text{obs}}$  values were plotted versus  $P$  in Fig. 8. The saturating pressure dependence of  $k_{\text{obs}}$  and the good reproducibility of equation (6) support the reaction scheme given in Fig. 7 for the surface oxidation process. The curve fitting analysis using equation (6) revealed that the  $K_A$  and  $k_1$  value was  $1.7 \times 10^{-6} \text{ Pa}^{-1}$  and  $51 \text{ s}^{-1}$  at room temperature, respectively.

#### 4. Conclusions

The surface oxidation process of the supported Ni(0) particle on SiO<sub>2</sub> have been investigated by *in-situ* XAFS and DXAFS method. The surface layer of the reduced Ni(0) particle was oxidized by the exposure to an O<sub>2</sub> atmosphere at room temperature. The oxidized portion was *ca.* 5 % of all Ni species, and the depth of the oxidized layer was estimated to be *ca.* 3 Å in considering the average particle size of 38 nm. The kinetic analysis revealed that the overall surface oxidation reaction is described by the dissociative adsorption equilibrium and the succeeding oxidation of the surface Ni(0) atom with the adsorbed oxygen. The proposed mechanism was supported by the saturating dependence of conditional first-order rate constants versus O<sub>2</sub> pressure.



**Fig. 8** The pressure dependence of  $k_{\text{obs}}$  for the surface oxidation process at room temperature.

#### Acknowledgment

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