Kinetic Study of Reduction Reaction for Supported PdO Species by Means of Dispersive XAFS Method

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Abstract. Time-resolved dispersive XAFS experiments have been performed to study the reduction reaction of supported PdO species on γ-Al2O3. It has been clarified that the reduction of PdO by H2 proceeds with a unique kinetic behavior, i.e., the initial part of the reduction is expressed by the first-order kinetics on Pd and the reaction order is changed to be zero as the progress of the reduction. The observation is different from that for the other supported metal oxides, for which the reduction is first order through the reaction. The reduction process of PdO is divided into the surface reduction to form the surface Pd(0) species and the succeeding oxygen exchange between inner PdO and surface Pd(0). When the latter step is faster than the former, the reduction rate of PdO is explained in terms of the zero-order kinetics. The pressure dependences of the conditional first- and zero-order rate constants suggest that the Langmuir-type molecular adsorption of H2 precedes the surface reduction of PdO particles.

1. Introduction
The supported Pd species are well known as useful active catalysts for various chemical reactions, such as hydrogenation, reforming, detoxification of toxic exhausts, etc [1]. The catalytic activity is largely affected by the chemical state, the particle size, and the interaction with the supporting material for the Pd species. It has also been reported that the Pd catalyst has higher activity at a partially reduced state of PdO [2]. The microscopic speciation and the mechanistic investigation in the atomic scale are thus important to understand the catalytic performance. The X-ray absorption fine structure (XAFS) is the most powerful analysis tool for such purposes, and its time-resolved spectroscopy can reveal the dynamic changeover of the active species in response to the reaction environments. Kinetic studies for the supported Pd species are essential to reveal the redox mechanisms and to understand the reactivity of the catalysis reactions. The clarified reaction mechanism may become a useful guide for catalysis design with the improved performance. In this study, we have focused on the reduction mechanism of PdO supported on γ-Al2O3, which is closely related to the preparation and activation of Pd catalysts.

2. Experimental
The 10 wt% Pd catalysts supported on γ-Al2O3 were prepared by the impregnation method. A mixture of acetone solution of palladium acetate and γ-Al2O3 was dried at 383 K for 12 h, and the obtained powder was calcined in air at 673 K for 3 h. The particle size of Pd with the radius distribution in the range of 4-11 nm was estimated by the transmitted electron microscopy after the reduction treatment.
The Dispersive XAFS (DXAFS) measurements were carried out at the NW2A beamline of PF-AR (KEK, Japan) to study the kinetics for the reduction of PdO with H\textsubscript{2}[3]. A Si(511) bent crystal (bend radius of 900 mm) was used as the Laue-type polychromator for the DXAFS instrument. The powder of Pd/\gamma-Al\textsubscript{2}O\textsubscript{3} was set in an \textit{in situ} DXAFS chamber. The chamber was first evacuated and the reaction gas (H\textsubscript{2} for reduction) was rapidly injected into the chamber. The DXAFS measurements were started just before the injection and the spectra were recorded with the time resolution of at most 10 ms. The quantity of injected H\textsubscript{2} molecules were in excess to the amount of Pd species, and thus the pseudo-first-order condition was ensured for PdO. Because the reduction by H\textsubscript{2} and oxidation by O\textsubscript{2} occurred reversibly, the initial PdO state was reproduced by the treatment with O\textsubscript{2} after the time-resolved monitoring for the reduction process. All DXAFS measurements were performed at 823 K.

3. Results and discussion

A representative spectral change and the extracted absorbance changes at 24.37 keV, which corresponds to the white line peak top of PdO, are shown in Fig. 1. The initial and final spectrum is perfectly in agreement with that of PdO and Pd, respectively, indicating that the redox reaction proceeds quantitatively and reversibly. The existence of some isosbestic points indicates that there are no observable metastable intermediates. Therefore, the relative X-ray absorbance shown in Fig. 1(b) is proportional to the content of the PdO species. Interestingly, it is found that the X-ray absorbance varies exponentially at the beginning of the reduction and then changes linearly. The reproducibility has been observed for this behavior, which is independent on the injection pressure of H\textsubscript{2}, the amount of sample powder, the loading of Pd, and the measurement temperature in the range from 400 to 600 °C. Such unique time-course changes are clearly different from the standard first-order kinetics which is represented by a single exponential function. Only a single-exponential or a linear function does not reproduce the observations, which are only explained in terms of a combination of first- and zero-order reaction kinetics as described below.

The reduction of PdO by H\textsubscript{2} is divided into three steps, \textit{i.e.}, the adsorption of H\textsubscript{2} (eq. (1)), the reduction of surface PdO (PdO\textsuperscript{\textcircled{\textminus}}) to generate surface Pd(0) (Pd\textsuperscript{\textsuperscript{\textcircled{\textsuperscript{0}}}}) as shown by eq. (2), and the O atom

![Figure 1](image-url). Time-resolved XANES spectra (a) for the reduction of PdO with H\textsubscript{2} and the absorbance change at 24.37 keV (b) under various H\textsubscript{2} pressures. The calculated curves are included in (b).
exchange between Pd\textsuperscript{*} and internal PdO (eq. (3)).

\[
H_2 + \text{PdO} \rightleftharpoons \text{PdO}^* + H_2
\]  
(1)

\[
\text{PdO}^* + H_2 \xrightarrow{k_1} \text{Pd}^* + H_2O
\]  
(2)

\[
\text{Pd}^* + \text{PdO} \xrightarrow{k_2} \text{PdO}^* + \text{Pd}
\]  
(3)

Because the PdO particles are quantitatively reduced on \(\gamma\)-Al\textsubscript{2}O\textsubscript{3} under the current experimental conditions, the sequential extraction (eq. (2)) and supply (eq. (3)) of O atoms at the particle surface is necessary to reduce the internal part of the PdO particle.

At the early stage of the overall reduction process, the Pd\textsuperscript{*} species is not considered to be sufficiently accumulated to proceed the oxygen exchange represented by eq. (3). The reaction rate is thus given by eq. (4) by neglecting eq. (3),

\[
-\frac{dN_{\text{PdO}}}{dt} = k_1N_{\text{PdO}}^*\theta_{H_2} = k_1\theta_{H_2}\alpha N_{\text{PdO}}
\]  
(4)

where \(N_x\) denotes the number of species \(x\), \(\theta_{H_2}\) is the coverage of adsorbed \(H_2\), and \(\alpha\) means the ratio of surface atoms for a PdO particle. The equation (4) indicates that the PdO reduction shows the first-order kinetics on Pd, i.e., the absorbance is changed exponentially vs. time. By accumulating the Pd\textsuperscript{*} species on the PdO particles, it has been found that the reaction changes to follow the zero-order kinetics on Pd. The diffusion of O atoms must play a key role in this stage. First, we suppose the steady-state assumption for the Pd\textsuperscript{*} species.

\[
\frac{dN_{\text{Pd}^*}}{dt} = k_1N_{\text{PdO}}^*\theta_{H_2} - k_2N_{\text{Pd}^*}N_{\text{PdO}} = 0
\]  
(5)

The total number \((N_{\text{Pd}^*})\) of surface Pd species is defined by eq. (6).

\[
N_{\text{Pd}^*} = N_{\text{PdO}} + N_{\text{Pd}^*} = \frac{k_1\theta_{H_2} + k_2N_{\text{PdO}}}{k_2N_{\text{PdO}}}
\]  
(6)

The reduction rate of PdO is then written as eq. (7) by using eqs. (5) and (6).

\[
-\frac{dN_{\text{PdO}}}{dt} = k_2N_{\text{Pd}^*}N_{\text{PdO}} = \frac{k_1k_2\theta_{H_2}N_{\text{PdO}}}{k_1\theta_{H_2} + k_2N_{\text{PdO}}}N_{\text{Pd}^*}
\]  
(7)

When the O atom exchange (eq. (3)) is faster than the surface reduction step (eq. (2)), eq. (7) is approximated to be eq. (8).

\[
-\frac{dN_{\text{PdO}}}{dt} \approx k_1\theta_{H_2}N_{\text{Pd}^*}
\]  
(8)

By assuming \(N_{\text{Pd}^*}\) as a constant vs. time, the reduction rate of PdO becomes independent on the number of Pd species, leading to the zero-order law for the Pd species. According to eqs. (4) and (8), the conditional rate constants in the early and later stage are then expressed by \(k_{1\text{obs}} = k_1\theta_{H_2}\alpha_{\text{pd}}\) and \(k_{2\text{obs}} = k_1\theta_{H_2}/N_{\text{Pd}^*}\), respectively.

The faster oxygen migration (eq. (3)) than the preceding surface reduction (eq. (2)) keeps \(N_{\text{PdO}}^*\) to be constant during the progress of the reduction. It is concluded that the apparently unchanged \(N_{\text{PdO}}^*\) causes the zero-order kinetics on PdO. This reduction mechanism is contrast to the other supported metal oxide, such as NiO, for which the reduction is first-order on the NiO species. The linearly aligned O atoms in the crystal structure of PdO\textsuperscript{[4]} may contribute to the faster oxygen migration rather than NiO with the rock salt structure \([5]\), in which the oxygen migration is inhibited by the alternatively arranged Ni atoms.

The conditional rate constants, \(k_{1\text{obs}}\) and \(k_{2\text{obs}}\), have been determined under various \(H_2\) pressures \((P_{H_2})\). The \(H_2\) pressure dependence of \(\theta_{H_2}\) is given by eq. (9) and (10) for the Langmuir-type molecular adsorption and the dissociative adsorption in terms of the corresponding equilibrium constant, \(K_{A}^{(m)}\) and \(K_{A}^{(d)}\), respectively.
The curve-fitting results are compared in Fig. 2 for the two adsorption models. It is found that the molecular adsorption model reproduces well the observed rate constants for both $k_1^{\text{obs}}$ and $k_2^{\text{obs}}$. In addition, the almost linear dependence shown in Fig. 2 indicates that the molecular adsorption equilibrium of H$_2$ is inclined to the left hand side under the high measurement temperature.

4. Conclusions
The solid-phase reduction of PdO particles supported on $\gamma$-Al$_2$O$_3$ has been clarified by means of the time-resolved DXAFS method. The unique kinetic behavior has been explained by the combined first- and zero-order rate law. The latter is interpreted in terms of a faster oxygen migration in the PdO particle than the surface reduction step. The H$_2$ pressure dependence of the rate constants reveals that the Langmuir-type molecular adsorption of H$_2$ precedes the surface reduction of PdO particles.

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