

Detailed Structural Analysis of Pd Particles through Use of XAFS and STEM-EELS in Tandem

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ABSTRACT

In order to realize more effective use of palladium, one of the precious metals employed in catalysts for the conversion of automobile exhaust gases, it is important to possess an understanding of the detailed structure of the metal particles. However, it has not proved easy to visualize the structure of palladium particles in three dimensions using individual analytic techniques. A detailed analytic technique was therefore created through the use of X-ray absorption fine structure analysis, scanning transmission electron microscopy and electron energy loss spectroscopy, and first principle calculations in tandem. The application of this analytic method made it possible to formulate a model of palladium particles incorporating nano-scale data. The formulated model showed that palladium oxide in three different valence states displays a unique structure, forming aggregates with microscopic clusters of approximately 3 nm as the minimum units.

1. Introduction

With the current worldwide growth of environmental awareness, demand is increasing for vehicles that achieve both low levels of exhaust emissions and high levels of fuel economy. The greater thermal efficiency realized in increasing the fuel economy of internal combustion engines reduces exhaust gas temperatures, necessitating increased low-temperature activation of three-way catalytic converters (TWC). At the same time, reduction of the volume of use and the realization of more efficient use of platinum (Pt), rhodium (Rh), and palladium (Pd), the precious metals employed in TWC, is a pressing issue from the perspective of avoiding resource risk. Honda has responded to the issue of avoiding resource risk by making effective use of Pd, the supply of which is comparatively stable. From the 2012 Accord onwards, Honda's catalysts have used no Pt and half the previous volume of Rh⁽¹⁾. The importance of Pd, which supplements conversion performance in order to make up for the reduction in Rh, is therefore increasing. In comparisons of single-element Pd and Rh catalysts (containing no other additive elements), while the catalysts display identical initial performance, the NO_x conversion performance of the Pd catalysts displays a particular decline following aging. This is believed to be due to

nano-scale changes in the structure of the Pd particles, which function as reaction sites for oxidation-reduction reactions of substances in the exhaust gas. The development of catalysts in which the Pd particles retain their structure even after aging is therefore considered to be an important focus in realizing the effective use of Pd. In order to do so, it will be necessary to obtain a detailed understanding of the nano-scale structure of Pd particles. If it were possible to model and visualize the initial structure of the Pd particles in three dimensions, it would become feasible not only to conduct reaction simulations and other simulations using accurate surface structures, but it could also be expected to be possible to propose highly active Pd particle shapes that could be retained following aging.

A number of research teams have previously reported on observation of the shape of supported Pd nano-particles using electron microscopy⁽²⁾⁻⁽⁴⁾, and studies of the microscopic behavior of Pd on carriers using synchrotron radiation analysis techniques⁽⁵⁾⁻⁽⁶⁾. X-ray absorption fine structure (XAFS) obtained using synchrotron radiation offers data concerning the average coordination environment around the element being focused on in an entire test material, but because the three-dimensional coordination environment is reduced to one dimension, the method offers insufficient spatial data, and it is not easy to realize a three-dimensional

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model structure through analysis of the obtained spectra alone. Analysis using scanning transmission electron microscopy and electron energy loss spectroscopy (STEM-EELS) makes it possible to obtain data concerning local structure on the nano-scale, but it is not possible to observe lattices when the particles under observation do not have a clear crystal structure, and said particles are also often damaged by the electron beam, making it necessary to exercise adequate caution during observations. In addition, the identification of metastable phases for which reference materials cannot be obtained using EELS spectrum analysis represents a challenge. As a result of these characteristics of the methods, no reports are available concerning the accurate modeling of the particle structures formed by supported Pd.

2. Aims

Because it was difficult to model Pd particle structure using either of the analytic techniques XAFS or STEM-EELS in isolation, it was necessary to create an analytic method by coupling the two techniques. First, one-dimensional data concerning average elemental defects and periodicity were obtained using XAFS, and compared with a cluster model in order to reflect atomic-level data in three-dimensional data concerning particle size and other parameters; a structural model was hypothesized in accordance with the results of STEM observation. This was compared with STEM-EELS results using spectrum simulations based on first principle calculations, in order to verify the validity of the abovementioned structural model. The development of this coupled analytic method made it possible to model Pd particles without inconsistencies.

3. Test Method

3.1. Manufacture of Test Materials

Because EELS uses transmission electron beams, analysis using the method is hindered if other particles exist in the background of those under observation. $\alpha\text{Al}_2\text{O}_3$ (99.9%; manufactured by Kojundo Chemical Laboratory Co., Ltd.), which has a simple geometry, was therefore selected as the carrier. Palladium nitrate (manufactured by Kojima Chemicals Co., Ltd.) was employed as the Pd precursor.

Palladium nitrate corresponding to 1 wt% of Pd was supported on $\alpha\text{Al}_2\text{O}_3$, following which it was calcined in air at 450°C for three hours in order to remove the nitric acid component. Below, the particles formed by Pd when supported on $\alpha\text{Al}_2\text{O}_3$ will be referred to as “unknown Pd particles.”

3.2. Test Apparatus

Employing a PF-AR NW10A beamline (Experimental Proposal Number: 2012G586) located at the High Energy Accelerator Research Organization’s Institute of Materials

Structure Science, the manufactured test material was studied via Pd K-edge XAFS using the transmission method. A Pd foil and palladium oxide (PdO) were employed as reference materials. REX2000 Ver. 2.5.9 (Rigaku Corporation)⁽⁷⁾ was used for extended X-ray absorption fine structure (EXAFS) analysis. The structural analysis functions of MedeA (Materials Design, Inc.) were employed in studying the coordination number of the modeled unknown Pd particles⁽⁸⁾.

The HD-2700 Cs-corrected STEM-EELS 200 kV manufactured by Hitachi High-Technologies Corporation was employed for STEM-EELS, and the CASTEP module of Material Studio Ver. 5.5 (Dassault Systemes Biovia) was employed for EELS spectrum simulations based on first principle calculations⁽⁹⁾⁻⁽¹¹⁾.

4. Results and Discussion

4.1. XAFS Analysis Results

An EXAFS analysis was conducted using the following steps in order to study the change ratio of the coordination number and the distance between the coordination elements for the unknown Pd particles.

- (1) Using McKale parameters⁽¹²⁾ based on spherical wave approximation, curve fitting was applied simultaneously to the nearest neighbor Pd and the next-nearest neighbor Pd atoms in the spectrum following Fourier transform of EXAFS of the Pd foil reference material. Analytic ranges for the forward baseline for the absorption edge (the pre-edge), EXAFS extraction, Fourier transform, and Pd foil curve fitting were set to help ensure that the results of the analysis converged on valid figures in comparison with the crystal structure of Pd foil⁽¹³⁾.
- (2) Curve fitting was applied simultaneously to the nearest neighbor O, nearest neighbor Pd [Pd (1)] and next-nearest neighbor Pd [Pd (2)] atoms in the spectrum following Fourier transform of EXAFS of the PdO reference material under the conditions described in Step (1). As in Step (1), the analysis ranges for pre-edge, EXAFS extraction, Fourier transform, and PdO curve fitting were again adjusted in order to help ensure that results for strength converged on valid figures in comparison with the crystal structure of PdO⁽¹⁴⁾.
- (3) With the analysis ranges from Step (2) as the initial values, the validity of the analysis ranges was studied by applying them to a further EXAFS analysis of Pd foil.
- (4) Steps (1) to (3) were repeated until analytic results for Pd foil and PdO matched the respective crystal structures with an error of no more than 1%.
- (5) Coordination numbers were set for each coordination sphere based on the bulk coordination numbers derived from the crystal structures of Pd and PdO, and Debye-Waller factors (indicators of thermal atomic oscillation and disturbance of the crystal structure) were derived.
- (6) The Debye-Waller factors for each coordination sphere of the unknown Pd particles were assumed to be

Table 1 Fitting results for Pd foil and PdO reference

	Coordination atom	Ideal values		Results		Change ratios	
		Coordination number	Coordination distance (nm)	Coordination number	Coordination distance (nm)	Coordination number (%)	Coordination distance (%)
Pd foil	Pd (1)	12	0.274	12.0	0.274	0	0
	Pd (2)	6	0.387	6.00	0.387	0	0
PdO reference	O	4	0.203	4.01	0.203	0.25	0
	Pd (1)	4	0.305	4.00	0.305	0	0
	Pd (2)	8	0.343	7.98	0.343	-0.25	0

identical to values for the reference materials, and the Debye-Waller factor values for the reference materials were set for subsequent analyses.

- (7) An analysis of the unknown Pd particles was conducted using the analysis range determined in Step (4).

Figure 1 shows the results of curve fitting for the Pd foil and PdO reference materials. Figure 2 shows the respective crystal structures, and Table 1 shows the parameters obtained. Test values and calculated values match well in the region of analysis, and there is a good correspondence between each parameter and values obtained from the crystal structures, with errors of less than 1%. Coordination numbers were set based on bulk coordination numbers, and Debye-Waller factors were derived under the applied

analytic conditions.

Figure 3 shows results for the PdO reference material and the unknown Pd particles following Fourier transform of EXAFS data. There is no significant difference in relation to nearest neighbor O atoms, but the peak strengths for nearest neighbor Pd and next-nearest neighbor Pd are lower for the unknown Pd particles, suggesting that a Pd elemental defect or a decline in periodicity due to a disturbance of the coordination distance or a reduction in particle diameter compared to bulk. The research then attempted to obtain results that would allow modeling of the unknown Pd particles by setting values for the reference

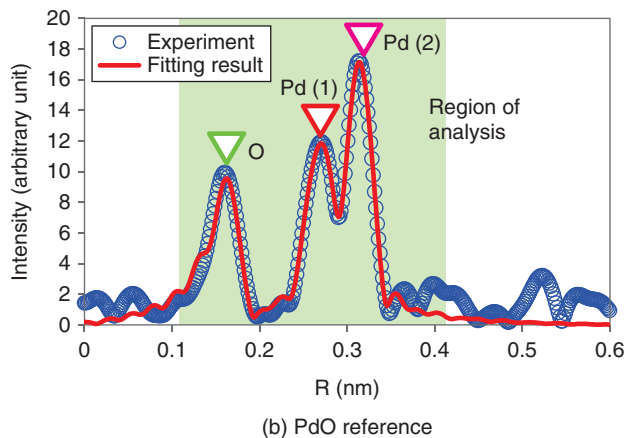
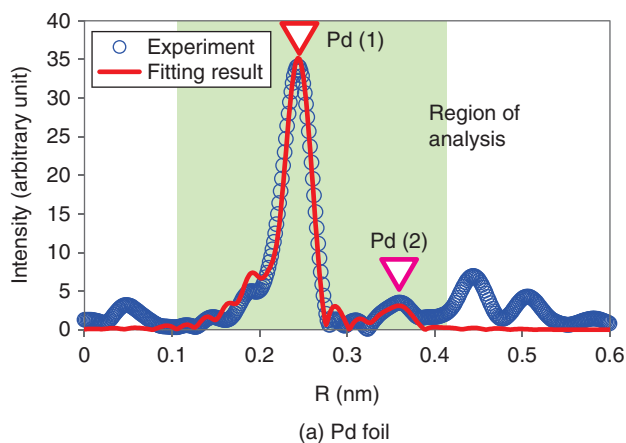


Fig. 1 Radial distribution functions and fitting results

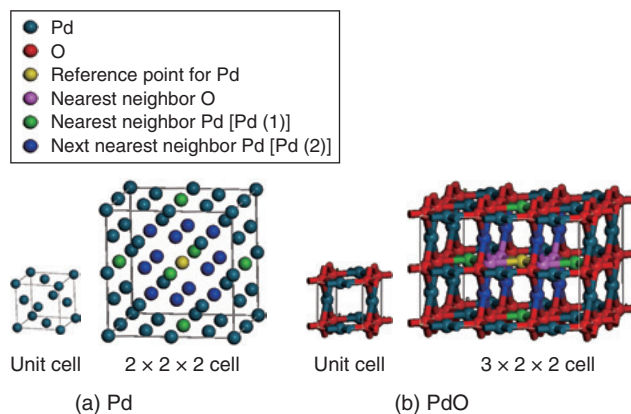


Fig. 2 Crystal structures and coordination environments of Pd and PdO

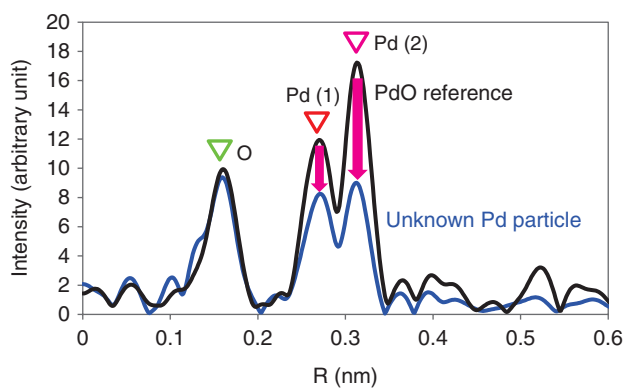


Fig. 3 Radial distribution functions for PdO reference and unknown Pd particle

Table 2 Fitting results for PdO reference and unknown Pd particle

Atom	PdO reference		Unknown Pd particle		Coordination number defect (%)	Change ratio of coordination distance (%)
	Coordination number	Coordination distance (nm)	Coordination number	Coordination distance (nm)		
O	4	0.203	3.68	0.204	7.9	-0.2
Pd (1)	4	0.305	3.27	0.304	18.3	0.1
Pd (2)	8	0.343	6.16	0.343	23.0	-0.1

material PdO as the values for the Debye-Waller factors and aggregating parameters for EXAFS strength changes as coordination numbers. Figure 4 shows curve fitting results for the unknown Pd particles, and Table 2 compares the parameters obtained from the analysis with the PdO reference material. The analysis of the unknown Pd particles was conducted in the same region of analysis as the analysis of the PdO reference material. Figure 4 shows that there is a good correlation between test values and calculation values.

The analysis results indicated that the bond length for the unknown Pd particles was the same as that for the PdO reference material, but that the coordination number for O was 8% lower, the coordination number for Pd (1) was 18% lower, and the coordination number for Pd (2) was 23% lower.

4.2. Modeling of Unknown Pd particles

The modeling of the unknown Pd particles proceeded according to the following steps, with comparison of cluster models based on the results obtained from XAFS analysis.

- (1) Multiple models with different cluster sizes were formulated based on the crystal structure model for the PdO reference material (Fig. 5).
- (2) The coordination numbers of the nearest neighbor O atoms, the nearest neighbor Pd atoms, and next-nearest neighbor Pd atoms were analyzed and plotted in relation to cluster size (Fig. 6).
- (3) Curve fitting was applied using cluster size and coordination number as functions.
- (4) Cluster sizes for each of the coordination elements

Table 3 Cluster size analysis results for unknown Pd particle

Coordination atom	Coordination number (experimental result)	Cluster size (nm)
O	3.68	3.0
Pd (1)	3.27	2.1
Pd (2)	6.16	2.1

were derived from the coefficients obtained in Step (3) and the coordination numbers obtained from the XAFS analysis results (Table 3).

- (5) The size of unit cells [Fig. 7(a)] was determined based on the amount of elemental defects obtained from the PdO reference material (Table 2), and Pd atoms were removed based on the cluster size obtained in Step (4) [Fig. 7(b)].
- (6) The structure produced in Step (5) was clustered to produce the same cluster size for O as obtained in Step (4) [Fig. 7(c)].

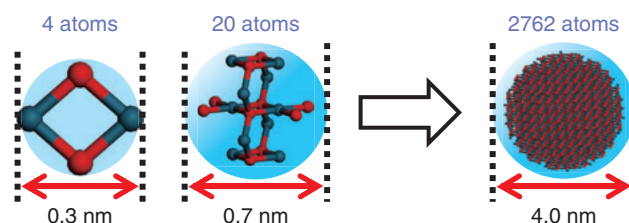


Fig. 5 Cluster models of PdO

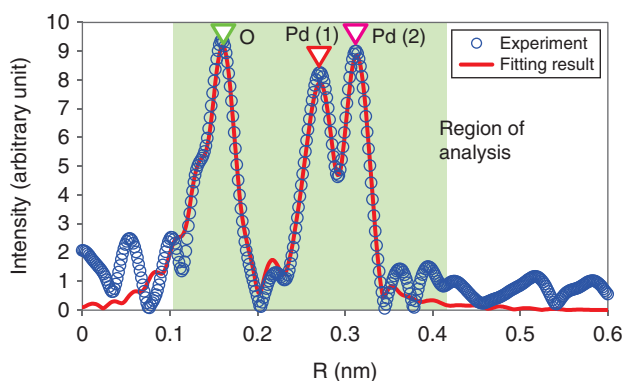


Fig. 4 Radial distribution function and fitting result for unknown Pd particle

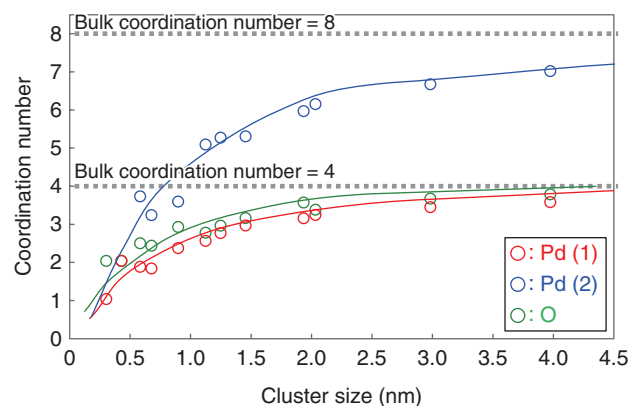


Fig. 6 Cluster size-dependence of coordination numbers for PdO

(7) Cluster models were formulated using the various combinations of positions of elemental defects in Steps (1) to (6); the respective coordination numbers were verified, and a model was selected in which there was no inconsistency with the results of XAFS analysis.

In the curve fitting of the coordination number and cluster size, Eq. (1) was employed to find the asymptotes to the bulk coordination numbers as the cluster sizes increased.

$$Y = N - A \times \text{EXP}(-X/\tau) \quad (1)$$

Here, Y is the coordination number for each element, N is the bulk coordination number, X is the cluster size, and A and τ are coefficients expressing the relationship between the coordination number and cluster size.

Figure 6 shows the results of curve fitting of coordination number and cluster size for each cluster model. The results indicate that Eq. (1) made it possible to basically reproduce the tendency of the results for coordination number and cluster size. Next, Eq. (2) was employed to derive cluster size from arbitrary coordination numbers.

$$X = -\tau \times \ln[(Y - N)/A] \quad (2)$$

When employing Eq. (2), coordination numbers derived from the EXAFS analysis were used for Y , and parameters derived from Eq. (1) were used for τ , N , and A . The cluster size estimated from the coordination number of O, X_O , was approximately 3.0 nm, and the cluster size estimated from the coordination numbers for Pd (1) and Pd (2), X_{Pd} , was approximately 2.1 nm (Table 3). The maximum cluster size was therefore approximately 3.0 nm.

Because there were numerous Pd defects and the Pd cluster size was lower than the O cluster size, modeling commenced by removing Pd. The unit cells in the PdO reference material were taken to be $2 \times 2 \times 2$ super cells, and, after Pd was removed to create areas equivalent to

Table 4 Modeling results for unknown Pd particle

Coordination atom	Coordination number (experimental result)	Coordination number (cluster model)	Change ratio of coordination number (%)
O	3.68	3.61	1.9
Pd (1)	3.27	3.19	2.4
Pd (2)	6.16	6.22	1.0

Table 5 Settings for calculation of EELS spectrum using CASTEP

Item	Setting
Functional	GGA PBE
Spin polarized	Checked (Use formal spin as initial)
Metal	Checked
Energy cutoff	610 eV
SCF tolerance	5.0×10^{-7}
k-point separation	0.04 1/Å
Pseudopotentials	On the fly
Energy range of core level spectroscopy	25 eV
Instrumental smearing	1 eV

cluster size X_{Pd} , O was clustered to produce the cluster size X_O . While referring to the structure obtained from STEM-HAADF observation (to be discussed below), the resulting clusters were randomly positioned, and a bulk model and a surface model of the unknown Pd particles were formulated [Figs. 7(d) and (e)].

The formulated cluster models corresponded well to XAFS analysis results, with change ratios of less than 2.5% (Table 4).

4.3. STEM-EELS analysis Results

Up to this point in the analyses, it had been predicted that the unknown Pd particles would display a variety of local structures as a result of elemental defects and differing cluster sizes. Because the formulation of reference materials displaying these local structures would represent a challenge, reference spectra for comparison with test results were formulated using first principle calculations, and employed to assist in making judgments in analyses of local structures. Measurements were conducted together with EELS spectrum simulations using the following process.

- (1) Multiple structures for Pd-O compounds were selected from the Inorganic Crystal Structure Database (ICSD).
- (2) Using CASTEP, EELS spectra were calculated for the K shells of the O atoms.

The unit cells employed in the calculation model were created by introducing core holes in single O atoms in $2 \times 2 \times 2$ super cells and resetting symmetry for each of the Pd-O compound unit cells selected in Step (1).

Table 5 shows the calculation conditions.

- (3) EELS spectra for O K-edge absorption were obtained from EELS spectrum measurements. Because irradiation with an electron beam over an extended period would

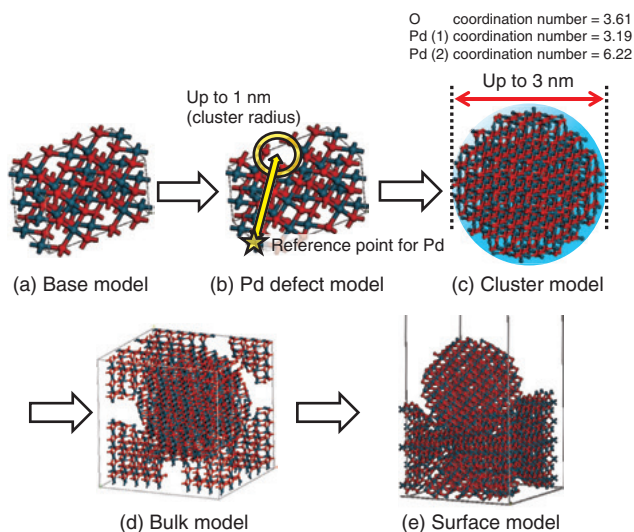


Fig. 7 Example of procedure for formulation of structural model of unknown Pd particle

change the shape of the particles, particular care was exercised in the measurements conducted to obtain EELS spectra; the authors attempted to obtain spectra within the measurement domain after adjusting the electron beam to near-field observation. When changes in the particle shape were observed following the measurements, the data was considered to be extrinsic local data, and fell outside the scope of the considerations.

- (4) Spectra obtained from tests and simulation results were compared, and candidates for local structures were identified.

Figure 8 shows a high-angle annular dark field (HAADF) image of the unknown Pd particles. Brightness in HAADF images increases in proportion with electron density, and areas in which heavy elements such as Pd are present and areas in which atomic density is high appear bright. The unknown Pd particles are distributed across a wide area, appearing to cover the $\alpha\text{-Al}_2\text{O}_3$, and a large number of particles of around 3 nm can be observed.

Figure 9 shows an example of the results obtained by identification of local structures through comparison of EELS spectra obtained in tests and the results of EELS spectrum simulations using first principle calculations. There is a good match between the test results and the results of spectrum simulations. Of 20 measurement areas, excluding six areas in which there was a change in the shape of the particles following measurements, local structures of the unknown Pd particles could be identified and broadly divided into three types as Pd_2O in five areas, PdO in six areas, and $\text{Pd}_{3.5}\text{O}_4$ in three areas.

The analysis demonstrated that the unknown Pd particles form aggregates of particles of around 3 nm, and display three types of local structure with different states of oxidation.

4.4. Validity of Model and Discussion

XAFS analysis suggested that the unit cluster size of the unknown Pd particles was approximately 3.0 nm; this matched the cluster size observed in STEM-HAADF images (Fig. 8).

In addition, a cluster model formulated to display no inconsistencies with the results of XAFS analysis showed local structures formed by different Pd oxides (Fig. 10), and this corresponded with local structure data obtained from EELS.

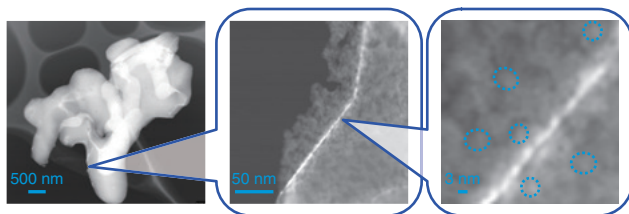


Fig. 8 STEM-HAADF image of unknown Pd particle

This model is backed up by XAFS, providing overall average structure data, and STEM-EELS results, providing local structure data, and represents a three-dimensional model of Pd immediately following support on a carrier.

This model shows that immediately following support

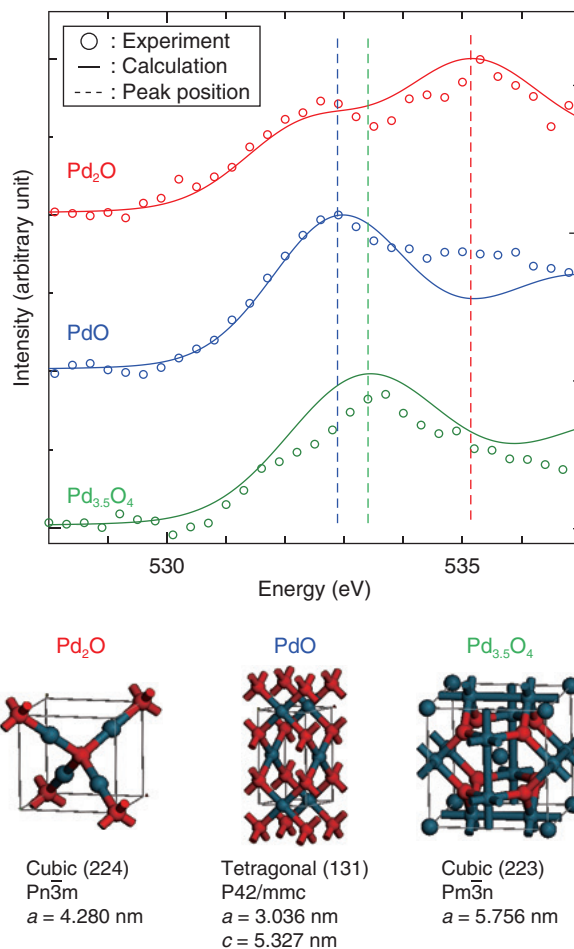


Fig. 9 EELS results for unknown Pd particle

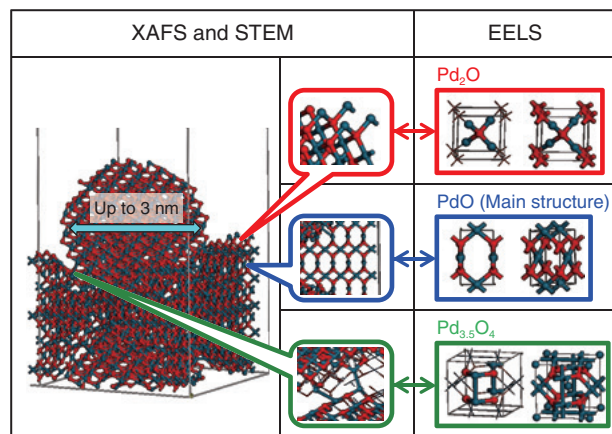


Fig. 10 Structural model based on XAFS, STEM and EELS

on a carrier, Pd forms aggregates of microscopic PdO unit clusters. Because of this, unlike bulk PdO there are gaps between clusters, and it can be conjectured that this makes it possible to actively move oxygen atoms in and out of the structure. Together with the fact that multiple valence states exist as local structures, this can be considered to indicate that immediately following support on a carrier, the Pd catalyst will display a high level of activity with regard to catalytic reactions for which oxidation-reduction reactions are essential.

This suggests that from perspectives other than maintaining the level of activity, maintaining microscopic PdO clusters that readily absorb and desorb oxygen and attempting to ensure the existence of multiple valence states as local structures represents one direction towards the effective use of Pd.

5. Conclusion

A direction for modeling unknown structures based on XAFS results obtained using synchrotron radiation has been established. The validity of the models was studied using STEM-EELS and EELS spectrum simulations based on first principle calculations in tandem. As a result, it was possible to determine a detailed structural model of unknown Pd particles supported on $\alpha\text{Al}_2\text{O}_3$, which had previously not been possible using the individual technologies.

The unknown Pd particles were shown to be structured from microscopic PdO clusters of around 3 nm, and displayed local structures produced by Pd in three different states of oxidation as a result of elemental defects within the clusters and on their surfaces.

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