

Compositions and structures of palladium oxide cluster ions studied by ion mobility mass spectrometry

○ M. A. Latif¹, Jenna Wu¹, Motoyoshi Nakano^{1,2}, Keiji Ohshimo¹, Fuminori Misaizu¹

¹ Graduate School of Science, Tohoku University

² Institute for Excellence in Higher Education, Tohoku University

[Abstract] Geometrical structures of palladium oxide cluster cations have been investigated by ion mobility mass spectrometry (IM-MS) and quantum chemical calculations based on density functional theory. Stable compositions of $(\text{PdO})_n^+$ ($n = 3-5$) were observed in a mass spectrum. Experimental collision cross sections (CCSs) of these clusters were measured from ion mobility spectrometry. Experimental CCSs of these cluster ions were compared with theoretical orientation averaged CCSs for optimized structures. As a result, the $(\text{PdO})_n^+$ clusters for $n = 3-5$ were assigned as compact structures containing molecularly attached oxygen.

[Introduction] The most well-known catalytic activity of palladium is CO combustion in automotive combustion system [1-2]. The function and activity of a specific oxidation catalyst are often governed by its size, morphology, structure and in addition by the chemical nature of catalyst surface, which may differ in the presence of oxygen from its bare state. Therefore, the oxidation process of Pd surfaces has been extensively studied for the model catalyst system [3]. Geometrical structures in particular the arrangement of different types of oxygen species on the Pd surface and its stability are therefore important to evaluate catalytic activity of the nano-sized model, such as cluster in the gas phase.

[Methods] A variety of series of palladium oxide cluster cations, Pd_nO_m^+ , were generated by a combination of laser vaporization and supersonic expansion of O_2/He mixture gas by using a home-built IM-MS apparatus. The generated cluster ions were injected into the ion-drift cell of ion mobility spectrometer (Figure 1) with a kinetic

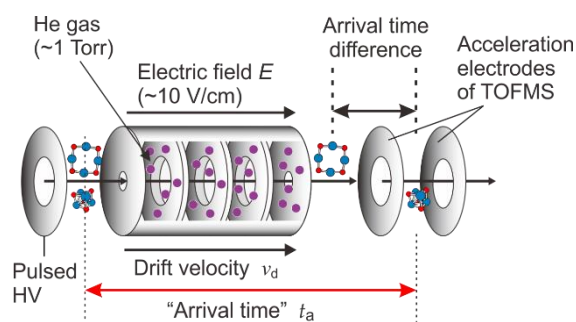


Figure 1. Ion-drift cell in IM-MS.

energy of 50 eV by a pulsed electric field. Due to a balance of acceleration of ions by an electric field and deceleration by collisions between cluster ions and buffer gas atoms, each cluster attains a constant drift velocity. Then the ions were reaccelerated by further pulsed voltage in an acceleration region of the time-of-flight (TOF) mass spectrometer at a given time later from the first pulse, arrival time. This arrival time is almost equal to the time in which an ion spends in the cell, and thus it depends on the CCSs of a cluster ion. Therefore, cluster ions with different CCSs reach the acceleration region of the TOF mass spectrometer

at different arrival time. By obtaining TOF mass spectra at different arrival times, arrival time vs. TOF 2D plot were obtained.

[Results and Discussion] The compositions of Pd_nO_m^+ cluster cations were obtained from the IM-MS measurement at 50 eV injection energy. A series of $\text{PdO}_{0.2}^+$, $\text{Pd}_2\text{O}_{0.4}^+$, $\text{Pd}_3\text{O}_{1.6}^+$, $\text{Pd}_4\text{O}_{2.8}^+$ and $\text{Pd}_5\text{O}_{3.8}^+$ cluster cations were observed at 50 eV injection energy (Figure 2). Among the species observed in the mass spectrum at 50 eV injection energy, the $(\text{PdO})_n^+$ series were showed as relatively high intensity due to the extra stability of bulk PdO, hence selected for structural assignment.

Meanwhile, arrival time distributions (ATDs), in which the total ion intensity of certain TOF peak was shown as a function of arrival time, were obtained from the 2D plot (Figure 3). With the information from the 2D plot, experimental CCSs were estimated by applying kinetic theory of ion transport [4].

On the other hand, some structures were obtained theoretically by B3LYP/LanL2DZ level in Gaussian 09, and their CCSs were calculated by projection approximation method in the MOBCAL program [5]. By comparison between experimental and theoretical CCSs, geometrical structures were determined. The structures containing molecularly attached oxygen were assigned as plausible structures for $n = 3-5$, of $(\text{PdO})_n^+$ series (Figure. 4).

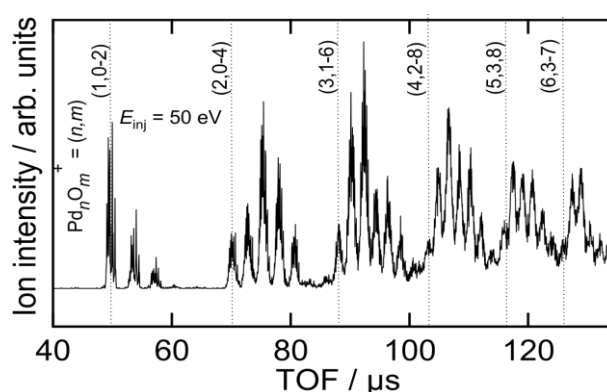


Figure 2. Mass spectrum of Pd_nO_m^+ cluster ions. Dashed lines indicate the initial peak of specific series.

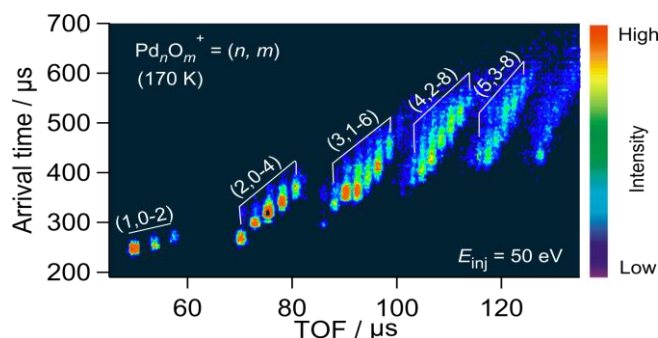


Figure 3. 2D plot of TOF vs. arrival time





























n	Optimized Structures of $(\text{PdO})_n^+$						
$\Omega_{\text{exp}} (\text{\AA}^2)$							
3 55.1 ± 1.1	 $\Omega_{\text{calc}} = 54.9$ $\Delta E = 0.0 \text{ eV}$	 54.0 (0.39)	 54.9 (0.50)	 55.0 (0.61)	 66.9 (1.08)	 54.9 (1.25)	 54.9 (1.25)
4 63.2 ± 1.3	 63.3 (0.00)	 67.3 (0.57)	 61.6 (0.71)	 61.8 (0.75)	 65.0 (0.76)	 68.9 (0.90)	 64.85 (1.63)
5 69.0 ± 2.1	 72.6 (0.00)	 70.6 (0.22)	 70.2 (0.29)	 75.9 (0.78)	 82.0 (1.01)	 68.7 (1.23)	 75.2 (1.39)

Figure 4. Optimized structural candidates of $(\text{PdO})_n^+$ ($n = 3-5$). Experimental CCSs are shown in left column. The corresponding theoretical CCSs and relative energies from the most stable structures $\Delta E/\text{eV}$ in parenthesis. Plausible structures are indicated by underline.

[References]

- [1] L. Croft, *Nat. Chem.* **2**, 1009 (2010).
- [2] H. S. Gandhi et al., *J. Catal.* **216**, 433 (2003).
- [3] D. H. Parker et al., *J. Vac. Sci. Technol., A* **8**, 2585 (1990).
- [4] E. A. Mason and E. W. McDaniel, "Transport Properties of Ions in Gases", John Wiley, New York, 1988.
- [5] M. F. Mesleh et al., *J. Phys. Chem.* **100**, 16082 (1996).