Kinetic and Morphological Studies of Palladium Oxidation in

\[ \text{O}_2-\text{CH}_4 \text{ Mixtures} \]

by

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Abstract

The oxidation of Pd single crystals: Pd(111), Pd(100) and Pd(110) was studied using Temperature Programmed Desorption (TPD), X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES), Low Electron Energy Diffraction (LEED) and Scanning Tunneling Microscopy (STM) as they were subjected to O₂ in the pressure range between 1 and 150 Torr at temperatures 600-900 K. The oxygen species formed during oxidation, the oxygen uptake dependence on the sample history, the Pd single crystal surface morphology transformations, and the catalytic methane combustion over Pd single crystals were investigated in detail.

The Pd single crystal oxidation proceeded through a three-step mechanism. Namely, (1) oxygen dissociatively adsorbed on Pd surface, forming chemisorbed oxygen and surface oxide; (2) atomic oxygen diffused through a thin surface oxide layer into Pd metal, forming near surface and bulk oxygen; (3) bulk PdO formed when a critical oxygen concentration was reached in the near surface region. The diffusion of oxygen through thin surface oxide layer into Pd metal decreased in the order: Pd(110)>Pd(100)>Pd(111). The oxygen diffusion coefficient was estimated to be around $10^{-16}$ cm² s⁻¹ at 600 K, with an activation energy of 80 kJ mol⁻¹. Once bulk PdO was formed, the diffusion of oxygen through the bulk oxide layer was the rate-determining step for the palladium oxidation. The diffusion coefficient was equal to $10^{-18}$ cm² s⁻¹ at 600 K and the activation energy was approximately 120 kJ mol⁻¹. The oxygen diffusion through thin surface oxide layer and bulk PdO followed the Mott-Cabrera parabolic diffusion law.

The oxygen uptake on Pd single crystals depended on the sample history. The uptake amount increased with the population of the bulk oxygen species, which was achieved by high oxygen exposure at elevated temperatures, for example in 1 Torr O₂ at above 820 K. Ar⁺ sputtering or annealing in vacuum at 1300 K depleted the bulk oxygen.

The Pd single crystal surface morphology was determined by the oxidation conditions: O₂ pressure, treatment temperature and exposure time. When bulk PdO was formed, the single crystal surface was covered with semi-spherical agglomerates 2-4 nm in size, which tended to aggregate to form a “cauliflower-like” superstructure. The single crystal surface area during oxidation, determined by integrating the STM image, experienced three major expansions in consistent with a three-step oxidation mechanism. The surface area on the oxidized single crystals increased in the order: Pd(110)<Pd(100)<Pd(111).

Only amorphous PdO was formed during the catalytic CH₄ combustion in excess O₂ over Pd single crystals. The benchmark turnover rate was determined to be in the range of 0.72-0.9 s⁻¹ on the (111), (100) and (110) surfaces at 160 Torr O₂, 16 Torr CH₄, 1 Torr H₂O and 600 K. The results suggested that CH₄ combustion was structure insensitive. The activation period observed for CH₄ combustion in which the initial turnover rate was lower than the steady state rate was attributed partially to the slow oxidation of Pd single crystals and partially to the surface area increase during the reaction. Carbon dissolution was observed only during CH₄ combustion in excess CH₄ but in excess O₂.

Key words: Palladium; Palladium oxide; Oxidation; Oxygen; Scanning tunneling Microscopy; PdO morphology; PdO surface area measurement; Turnover rate for methane combustion.
Extended Abstract

Palladium is the best catalyst for the complete combustion of methane. However, practical challenging issues still remain that need to be resolved to allow for a better catalyst performance. These issues include: How does oxygen interact with palladium? Which is more active for the reaction, Pd metal, chemisorbed oxygen on Pd or PdO? What causes the catalyst activation? Is the reaction sensitive to the palladium surface structure? To resolve these issues, the oxidation of Pd catalysts and the catalytic CH₄ combustion in excess O₂ were studied in this research on Pd single crystals: Pd(111), Pd(100) and Pd(110).

To simulate the practical catalytic reaction, the oxidation of Pd single crystals was investigated as they were subjected to oxygen in the pressure range between 1 and 150 Torr at temperatures 600-900 K for varying exposure time 1-180 min. The oxygen uptake on the single crystals was determined by Temperature Programmed Desorption (TPD); the surface oxidation state was detected by X-ray Photoelectron Spectroscopy (XPS); the surface chemical composition was determined using Auger-electron Spectroscopy (AES); the change in the crystal lattice structure during the oxidation was monitored with Low Energy Electron Diffraction (LEED) and the Pd surface morphology transformation was imaged using Scanning Tunneling Microscopy (STM). The experiments were performed in a three-chamber UHV system. The Pd oxidation was carried out in the high-pressure reaction cell, and then the sample was transferred to the STM chamber and the analysis chamber for surface analysis.

The oxidation of Pd single crystals proceeded through a three-step mechanism. Namely, (1) O₂ dissociatively adsorbed on Pd surface, forming chemisorbed oxygen and then surface oxide; (2) atomic oxygen diffused through a thin surface oxide layer into Pd metal, forming near surface and bulk oxygen; (3) bulk PdO formed when a critical oxygen concentration was reached in the near surface region.

Dissociative adsorption of O₂ on Pd single crystal surfaces resulted in the p(2×2) oxygen overlayer on Pd(111) with the saturation coverage of 0.25 ML; the p(2×2) and/or c(2×2) oxygen overlayer on Pd(100) with the saturation coverages of 0.25 ML and 0.5 ML; and the c(2×4) reconstructed oxygen overlayer with the coverage of 0.5 ML. A higher oxygen coverage could be reached either by O₂ treatment under high pressure and/or temperature or by dosing to a stronger oxidant such as NO₂. Two-dimensional surface oxide, characterized by a complex LEED pattern distinct from that of PdO or the original metallic face, was formed by exposure of the (111) and (110) surfaces to 12 L NO₂ at 500-550 K. The (√5×√5)R27° oxygen overlayer, similar to PdO(001), was formed on Pd(100) surface under the same condition. The maximum coverage of 1.8 ML on Pd(110) and 0.8 ML on Pd(100) could be achieved by both O₂ and NO₂ dosing, but on Pd(111), the maximum coverage of 2.4 ML was only attainable after NO₂ exposure. This result suggested that both Pd(110) and Pd(100) are more reactive towards O₂ than Pd(111).
The diffusion of oxygen through a thin surface oxide layer into Pd metal became energetically feasible when the oxygen uptake increased beyond the surface saturation coverage. After an exposure of the Pd single crystals to 1-10 Torr O₂, two types of dissolved oxygen species were detected: (1) the oxygen species located in the near surface region was characterized by a TPD peak at approximately 800 K; (2) the bulk oxygen gave rise to a TPD peak above 1050 K.

The rate for the diffusion of oxygen into Pd near surface region decreased in the order: Pd(110)>Pd(100)>Pd(111). The oxygen uptake was approximately inversely proportional to the surface Pd atom densities. At this stage, bulk PdO was not formed; the oxygen uptake on the single crystals increased with the O₂ gas phase pressure; the O/Pd atomic ratio was less than 0.05 based on AES data; and a diffuse Pd (1\times1) LEED pattern from the metal substrate could be observed. The oxygen diffusion was well described by the Mott-Cabrera parabolic diffusion law. The diffusion coefficient was estimated to be \(10^{-16} \text{ cm}^2 \text{ s}^{-1}\) at 600 K with activation energy of approximately 80 kJ mol\(^{-1}\) on the three single crystals.

The diffusion of oxygen into the Pd bulk region was distinguished after high oxygen exposure at elevated temperatures, for example in 1 Torr O₂ at above 820 K. The oxygen uptake on Pd single crystals depended on the existence of bulk oxygen. After exposing the Pd(111) surface to 1 Torr O₂ at 700 K for 10 min, 26 ML of oxygen uptake was detected on a sample free of bulk oxygen; whereas 38 ML was determined on the sample populated with the bulk oxygen species. Ar\(^+\) sputtering or annealing in vacuum at 1300 K depleted the bulk oxygen.

Bulk PdO was formed when a critical concentration of oxygen was reached in the near-surface region. The oxide nucleation started in the vicinity of steps. The formation of bulk PdO was characterized by TPD with a considerably dropped oxygen uptake rate; no LEED pattern except for the bright background; O to Pd atomic ratio close to 0.3-0.7 detected using AES; and the shift in the core level Pd 3d\(_{5/2}\) peak by 1.8 eV determined with XPS. At this stage, the diffusion of oxygen through the bulk oxide layer was the rate-determining step for the oxidation of Pd. The diffusion coefficient was equal to \(10^{-18} \text{ cm}^2 \text{ s}^{-1}\) at 600 K and the activation energy was approximately 120 kJ mol\(^{-1}\). The oxygen diffusion in bulk PdO also followed the Mott-Cabrera parabolic diffusion law.

The transformation of Pd single crystal surface morphology during oxygen exposure depended on the oxidation conditions: O₂ pressure, treatment temperature and exposure time. On Pd(111): Monatomic cavities, islands and peninsulas appeared after exposure of the Pd(111) surface to 1-10 Torr O₂ at 600 K for 10 min; the step height gradually increased with O₂ pressure. After 1 and 10 Torr oxygen treatment, the step height was measured to be 2.45 \(\pm\) 0.1 Å, which was almost 9% higher than the steps on the clean Pd(111) surface. And after 25 Torr treatment, the step height was 2.6 \(\pm\) 0.1 Å, about 14% higher than the theoretical monatomic step height. This result indicated the expansion of the lattice structure due to accommodation of the interstitial oxygen atoms.
agglomerates nucleated and grew on the terraces after 25 Torr of O₂ treatment. After 50 Torr exposure, atomic steps were not distinguishable and the surface was covered with semi-spherical agglomerates 2-4 nm in size, which tended to aggregate to form a “cauliflower-like” superstructure. On Pd(100): exposure to 1 Torr O₂ at 600 K for 10 min led to the growth of islands on the terraces or out of the original step edges. The inter-planar spacing for the first two surface layers was expanded by 0.1-0.4 Å. Semi-spherical oxide agglomerates oriented along the steps nucleated and grew on the (100) surface after oxidation in 5-25 Torr O₂ at 600 K. The formation of bulk oxide in 50-150 Torr O₂ was characterized by a roughened amorphous “cauliflower-like” surface structure aggregating semi-spherical agglomerates approximately 2.8-3.5 nm in size. On Pd(110): a mesoscopic island structure was formed on Pd(110) surface after exposure to 1 Torr O₂ at 600 K for 10 min. Pressure increase to 5-25 Torr resulted in the nucleation and growth of rod-shaped agglomerates along <1̅10> with aspect ratio 2.5-4:1. After exposure to 50-150 Torr O₂, the elongated agglomerates rounded up and aggregated to reveal an identical oxide surface structure as observed on the Pd(111) and Pd(100) surfaces.

The surface area of Pd single crystals after oxygen treatment was measured by ¹⁸O isotope exchange and by STM image analysis. The two methods agreed within ±20%. It was found that the Pd single crystal surface area increased after oxidation, which transformed the Pd metal to PdO. After oxidation in 150 Torr O₂ at 600 K for 30 min, the surface area for Pd single crystals increased by a factor of approximately two and in the order of: Pd(110)<Pd(100)<Pd(111). This might be due to the fact that in order to accommodate stoichiometric amounts of oxygen, the close packed Pd(111) surface, which contains the highest density of palladium atoms on the surface, must expand more than the more open Pd(110) surface. Reduction in H₂ decreased the surface area of pre-oxidized Pd single crystals. An amorphous metallic surface was produced after complete H₂ reduction at 373 K, whereas a smooth surface with characteristic single crystal features was observed after reduction at 673 K.

An oxygen uptake hysteresis was found during exposure a Pd(111) surface to 1 Torr O₂ for 10 min in a temperature window from 820 K to 900 K. A large amount of oxygen dissolved in Pd if the sample was pre-heated in O₂ from room temperature to the exposure temperature; whereas, no oxygen uptake was detected when the sample was pre-heated in vacuum.

Catalytic combustion of methane in excess O₂ was studied over Pd single crystals in 160 Torr O₂, 16 Torr CH₄, N₂ balance to 800 Torr at 600 K for 60 min. After reaction, the three oxidized single crystals showed a similar amorphous PdO surface morphology, which did not correlate with the original orientations. A clear “cauliflower-like” structure 20 ± 5 nm in size appeared on the Pd surfaces. These large domain structures were composed of small semi-spherical oxide agglomerates around 4 nm in diameter. The surface area increase on the (111), (100) and (110) surfaces was 3.2, 2.2, and 1.6 respectively. Due to the absence of impurity and support effects, the benchmark turnover rate was determined to be in the range of 0.7-0.9 s⁻¹ on Pd(111), Pd(100) and Pd(110) surfaces, at 160 Torr O₂, 16 Torr CH₄, 1 Torr H₂O and 600 K. The turnover rate was
independent to the original orientation of the Pd single crystals where PdO grew from. Thus, it was suggested that the catalytic CH$_4$ combustion is structure insensitive to the oxidized Pd single crystal catalysts. Methane combustion on palladium single crystals experienced an activation period in which the initial nominal turnover rates based on the metal surface area were only about 1/8-1/4 of the steady-state rates based on the oxide surface area. This activation period was attributed to the slow oxidation of palladium single crystals and the surface area increase during reaction. Carbon dissolution into palladium bulk was found during methane combustion under reaction condition in excess methane (CH$_4$:O$_2$ = 10:1) but not in excess oxygen. Removal of the dissolved carbon required cycles of high-pressure oxygen exposure, for example 1 Torr at 780 K, followed by flashing at high temperature up to 1000 K.

Key words: Palladium; Palladium oxide; Oxidation; Oxygen; Scanning tunneling Microscopy; PdO morphology; PdO surface area measurement; Turnover rate for methane combustion.
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Chapter

1 Motivation
1.1 Palladium and catalytic methane combustion

Palladium, first isolated in the year of 1803, has proven to be an excellent catalyst for several types of reactions in the form of both element and compounds. In heterogeneous catalysis palladium is mainly used for hydrogenation and oxidation reactions. A promising application of palladium and its oxide as heterogeneous catalyst involves complete catalytic methane combustion in excess oxygen for energy generation in advanced gas-powered turbines and the abatement of methane emissions in the exhaust gas stream.

Methane, CH₄ is the “greener” of the fossil fuels. It has the highest hydrogen to carbon ratio in all hydrocarbons and thus could produce the highest amount of energy per CO₂ formed when burning. Meanwhile, many of the large reserves of natural gas, which is composed mainly of methane, have only trace content of impurities such as sulfur and nitrogen compounds. As a consequence, when the natural gas is burned, the emission gases will contain a low concentration of SOₓ and NOₓ formed from S and N compounds.

Combustion of methane could be achieved through conventional flame combustion in the gas phase or via catalytic reaction on the solid catalyst surface referred as catalytic methane combustion. As compared with the flame combustion, catalytic combustion takes the advantage of solid catalyst that lowers the activation energy to break the C-H bond and thus reduce the operating temperature. This advantage becomes more and more economically and environmentally valuable with the increasingly stringent regulation for the thermo-generated NOₓ emission level for energy generation turbines using natural gas as fuel. Conventional turbines (Figure 1.1) produce large amounts of NOₓ because of the
high adiabatic combustion temperatures in excess of 1800 °C [1]. At this temperature, the concentration of NO\(_x\) in the turbine exhaust could reach as high as 165 ppm (Figure 1.2). In comparison, catalytic combustion gas turbines (Figure 1.3), operated at around 1300 °C, dramatically reduce the NO\(_x\) formation to below 5 ppm (Figure 1.2) [2-4].

It has been reported that Pd based catalysts exhibit the highest turnover rate for catalytic CH\(_4\) combustion [5], and as compared to other transition metal catalysts for example Pt/Rh, Pd catalysts are more economical [6]. Recently the application of Pd-based catalysts has been scaled up on commercialized catalytic combustors [3, 6, 7].

1.2 Research objectives

Despite the industrial importance of Pd-based catalysts, a number of challenging questions however remain, which should be resolved to allow for a better catalyst performance in practical implementations. The issues to be studied in this research are outlined as follows.

1.2.1 Palladium oxidation mechanism

It has been recognized that palladium presents unusual situation in that the thermodynamically stable phase could be either Pd metal or Pd oxide depending on the oxygen partial pressure in the gas phase and the temperature. In air at atmospheric pressure, PdO is the active phase up to 1052 K, while above this temperature, Pd metal is stable [8-10]. As a consequence, Pd catalysts might present different active phases and experience the phase transition between metal and oxide along the catalytic combustion reactor bed due to the wide operating temperature range of 350-1300 °C (Figure 1.3).
Typically in the conditions when oxide phase is favored, Pd is oxidized to form PdO in the reaction atmosphere. The Pd oxidation mechanism should be identified.

The interaction of Pd single crystals with O$_2$ in low pressure especially below $10^{-6}$ Torr has been studied extensively in previous work, see for example [11-27] and references therein. Chemisorption of oxygen atoms on Pd single crystals results in the p(2\times2) overlayer with 0.25 ML coverage on Pd(111) [12, 24], p(2\times2) and c(2\times2) overlayers on Pd(100) with 0.25 and 0.5 ML coverages [13, 27], and the reconstructed c(2\times4) superstructure on Pd(110) with 0.5 ML coverage [18, 22]. The oxygen uptake beyond the saturation coverage could be reached for example, 2.4 ML on Pd(111), 0.8 ML on Pd(100) and 1.8 ML on Pd(110) by dosing stronger oxidants such as NO$_2$ [12, 13, 25] or exposing to O$_2$ in high pressures at high temperatures [11, 21, 22]. Accommodation of extra oxygen atoms requires the compression of the adsorbate layer that reduces the oxygen binding energy and then makes the penetration of adsorbed oxygen into subsurface region become energetically favorable [20]. The interactions between the oxygen and Pd atoms in the surface layers and the underlying Pd atoms lead to the formation of two-dimensional surface oxide [12]. The intermediate surface oxide observed on Pd(111) [11, 12] and Pd(110) [17, 28] presents a complex crystal structure distinct from that of PdO or the original metallic facets. While on Pd(100), the surface oxide appears to have a structure close to PdO(110) and PdO(001) [13, 27]. The surface oxide on Pd(111) forms monoatomic step height islands and peninsulas in the vicinity of steps. Removal of the oxide layer by reduction in CO [21] or annealing at 623 K [19] results in the formation of hexagonal 1 ML deep holes.
Despite the intensive studies on the interaction of Pd with O$_2$ at low pressure, the oxidation of Pd under realistic CH$_4$ combustion conditions, which is of particular interest for the industrial application, has not been well investigated. Therefore, in this study, the palladium oxidation mechanism was investigated when exposing Pd single crystals to O$_2$ in the pressure range of 1-150 Torr, at elevated sample temperature 600-900 K for extended oxidation time between 1 and 180 min.

1.2.2 Surface state changes by treatment in oxygen

Oxidation reaction modifies the Pd-based catalyst surface. Transmission Electron Microscopy (TEM) studies by Chen and Ruckenstein [29] and Ellipsometric studies by König et al. [30] and Graham et al. [31] reported the growth of highly porous PdO layers upon heating supported Pd crystallites or Pd film in O$_2$ and/or in catalytic CH$_4$ combustion atmosphere under rich conditions (CH$_4$:O$_2$ = 1.5:1). Oxidation of Pd crystallites in O$_2$ at 500 °C for 24 hrs led to the extensive development of the porous structures and eventually to the formation of cavities of different sizes on Pd crystallites [29]. This effect was assigned due to the low interfacial tension of PdO, which generated pits on the crystallites while spreading over metal and drove the pits to coalesce into large cavities [29]. Studies on complete methane combustion on Pd foil model catalyst by Monteiro et al. [32, 33] also indicated that Pd foil surface was roughened in the CH$_4$ oxidation reaction atmosphere. Using $^{18}$O$_2$ isotope exchange method, an increase in the surface area of approximately two fold was determined when the CH$_4$ combustion reaction was carried out in excess O$_2$ (O$_2$:CH$_4$ = 10:1), and of eighteen fold when the reaction was performed in excess CH$_4$ (CH$_4$:O$_2$ = 10:1). The extreme roughness resulted from CH$_4$ combustion under rich condition was confirmed with Scanning Electron
Microscopy (SEM) [33]. Using H₂-O₂ titration method, Ribeiro et al. [34] found the increase in Pd surface area by a factor of 2.7 after oxidation of a Al₂O₃ supported Pd catalyst and a factor of 2.5 of a ZrO₂ supported Pd catalyst in air at 973 K for 24 hrs.

To get a further understanding of the surface morphology transformation of Pd catalyst during CH₄ combustion and how the surface changes influence its catalytic activity, in this research, experiments were performed to characterize the surface morphology changes, surface chemical state changes and surface chemical composition changes during oxidation in O₂ and in CH₄ combustion atmosphere using Scanning Tunneling Microscopy (STM) along with X-ray Photoelectron Spectroscopy (XPS) and Auger-electron Spectroscopy (AES).

1.2.3 Dissolution of oxygen in Pd metal during O₂ oxidation

The dissolution of oxygen into Pd metal to form subsurface and bulk oxygen has been a focus of recent studies. Temperature Programmed Desorption (TPD) studies by Conard et al. [24] suggested a desorption-peak-maximum shift towards high temperature above 1100 K after an exposure of Pd(111) to 300 L of O₂ at 1045 K. This high-temperature shift was then assigned due to the dissolution of oxygen in Pd metal followed by bulk diffusion [24]. After exposing a Pd polycrystalline film to O₂ under a pressure far below the dissociation pressure of the oxide phase at a certain temperature, for example 3.5 × 10⁻² Torr at 1023 K, Campbell et al. [35] detected a substantial amount of oxygen uptake about 350 monolayers (1 monolayer ≈ 2 × 10¹⁵ atoms cm⁻²). This high amount of oxygen was suggested to dissolve into Pd metal bulk and make up of a Pd-O solid solution PdOₓ. More recently, Leisenberger et al. [20] reported that the penetration of oxygen into
subsurface region occurred upon oxygen adsorption at temperature above 523 K on Pd(111) surface. And according to Weissman et al. [36], the subsurface oxygen reservoir was mostly populated by high oxygen exposures at sample temperature of around 1000 K. Desorption of the subsurface oxygen species peaked at 1142 K [20]. The rate for oxygen diffusion into the subsurface region depends on the catalyst history. It was shown by Meusel et al. [37, 38] that less oxygen was initially available to the surface reaction for CO oxidation on supported Pd nano particles. Only after the subsurface oxygen reservoir was built up, stable reaction rate could be detected. Comparing to that on Pd single crystals, the oxygen incorporation into subsurface region started at much lower temperature around 300 K, and with stronger intensities on densely defected Pd nano particles [37, 38].

Subsurface oxygen species is not a simple passivating diffusion barrier, but influences both the dynamics of adsorbates and chemical reactivity of the surface. The migration of subsurface oxygen could induce the local expansion of Pd(111) atoms and the distortion of the host lattice as well as the relaxation of the topmost interlayer spacing [39, 40]. Rose et al. [40] proposed that subsurface oxygen could lower the energy barrier for dissociation and serve as active sites for surface reaction. This hypothesis was recently tested by Bondzie et al. [41], who identified the subsurface oxygen on Pd(111) as a nucleation of an oxide phase.

1.2.4 Dissolution of carbon in Pd metal during CH₄ combustion

Carbon is also found to dissolve in Pd metal bulk to form a Pd-C solid solution also referred as PdCₓ phase. The content of carbon could reach as high as 13-15% after an
exposure of palladium in an atmosphere of C₂H₄, C₂H₂ or CO [42, 43]. Catalytic CH₄ combustion over Pd foil under rich condition (CH₄:O₂ = 10:1) also led to the carbon dissolution as suggested by the TPD studies by Monteiro et al. [33]. Other procedures, such as deposition of Pd particles on carbon supports [44, 45] or evaporation of Pd on carbon thin film substrates [46] would result in the carbon dissolution as well. The dissolved carbon occupies the metal octahedral sites [42, 44] and expands the crystal structure. The Pd lattice parameter determined by X-ray diffraction (XRD) is increased by about 2.8% with a carbon concentration of 13% [47]. Even trace amount of carbon on the Pd single crystal (110) surface could cause an outward expansion of the inter planar spacing about 4% for the first 3-4 surface layers [46]. The presence of carbon either on the Pd surface or in the bulk has profound effects. Pd foil treated by catalytic CH₄ combustion under rich condition has a significant surface area increase of 18-fold compared with the 2-fold increase under lean condition (CH₄:O₂ = 1:10) [33]. Ellipsometric studies by König et al. [30] and Graham et al. [31] reported the growth of highly porous PdO layers upon CH₄ combustion under rich condition (CH₄:O₂ = 1.5:1) comparing to the dense layers formed under lean condition (CH₄:O₂ = 1:4). It is also found that carbon dissolution could suppress the chemisorption of hydrogen, oxygen and CO, reduce the ability to form Pd hydride (β-PdH₃), increase the heat of adsorption for hydrogen on Pd, while reduce that for CO [44, 45]. The recovery of the clean Pd phase from carbon contaminations is suggested to be achieved by heating in inert atmosphere at 870 K or in vacuum at 600 K [42, 47], in reduced atmosphere for example H₂ at 420 K [42, 48], or in oxidized atmosphere (O₂) to 420 K [42, 45].
In this study, the dissolution of oxygen during oxidation in O₂ and the dissolution of carbon during catalytic CH₄ combustion into palladium metal were investigated with labeled oxygen (¹⁸O₂) and methane (¹³CH₄) to seek for the conditions at which the oxygen and carbon dissolution occurred.

1.2.5 Activation of Pd catalyst for CH₄ combustion

CH₄ combustion over Pd supported catalysts often requires an activation period before a steady state reaction rate is reached. In the literature, this behavior has been suggested due to the presence of impurities [49, 50], the interaction with supports [51], the transformation between different sample oxidation states [52, 53], or the morphology change of Pd crystallites [54]. However, almost no activation period for CH₄ combustion over a Pd polycrystalline foil was detected in a previous research work by our group [32]. This current research was performed to investigate the catalytic CH₄ combustion over Pd single crystal catalysts in lean conditions. Special attention was focused on the initial stage during the reaction to seek the evidence for the catalyst activation.

1.2.6 Reaction sensitivity to surface structure

A question of practical and scientific interest is the relationship between structure and turnover rate of a catalyst. In other words, does the turnover rate change as the structure of the catalyst is changed? The question of structure sensitivity for CH₄ combustion over Pd catalyst typically in the condition when PdO is the active phase is an issue not yet resolved. Cullis and Willatt [55] found that the reaction was independent of particle size. Baldwin and Burch [54] found a change in turnover rate of two orders of magnitude on a series of catalysts with no correlation between particle size and turnover rate. Hicks et al.
[52, 53] found that the turnover rate was higher for larger Pd particles. Garbowski et al. [56] concluded that the reaction was structure sensitive by concluding from TEM analysis that some of the less packed planes Pd(100) and Pd(110) are more active than the more packed ones Pd(111). Ribeiro et al. [34] found that for supported catalysts with particles in the range 1-10 nm, different supports, and prepared with different metal precursors the rates were the same. More recently Fujimoto et al. [57, 58] on Pd/ZrO₂ and Müller et al. [59, 60] on Pd-Zr alloys found a ‘weak’ (factor of 3-9) structure sensitivity as the particle size varied from 4 to 10 nm.

Noteworthy that most of the literature results were obtained on supported catalysts. A number of factors thus could affect the data, especially the interaction between supports and the catalyst, which might change with time-on-stream and different catalyst preparation procedures. The few orders of magnitude difference in the reported turnover rates [34] could be interpreted due to the characteristic behavior of the Pd-supported system. Part of the problem could be the activation and deactivation observed on supported Pd and the fact that these effects did not correlate with changes in the Pd metal surface area. To address this question properly, Pd single crystal catalysts will be the ultimate choice. It is free of impurities, has no support effects and no internal heat and mass transfer limitations, in addition, it is easy to track the surface area changes during the oxidation reactions with surface science techniques. In this study, the kinetic data were obtained on the three lowest index Pd single crystals: Pd(111), Pd(100) and Pd(110) in the conditions when PdO was the active phase. By comparing the kinetics, the answer to the structure sensitivity of CH₄ combustion over PdO catalyst was reached.
1.3 Planar model catalyst

Research on real heterogeneous catalysts is often constrained by the poor accessibility to the complex structures of active particles on supports. To overcome this problem, planar models of supported catalysts are used. These include single crystals, foils, and metal particles deposited on planar oxides [61, 62]. Since planar model catalysts have all their area exposed at the surface, all the catalytic active area is accessible to powerful surface science techniques. In addition, catalytic reactions can be carried out in-situ under identical conditions as that for supported catalysts [63]. Thus no adjustment is necessary for the interpretation of the data and a correlation between structure and catalytic activity can then be derived more straightforward. In this research, the experiments were mainly carried out on the three lowest index Pd single crystals: Pd(111), Pd(100) and Pd(110). The research over the model catalyst with metal particles on planar oxides was proposed for future work.

1.4 Research outline

The research involves the following three topics:

1. Oxidation of palladium single crystals;

2. Surface area increase by subjecting to O\textsubscript{2} oxidation and CH\textsubscript{4} combustion;

3. Catalytic CH\textsubscript{4} combustion over Pd single crystal catalysts.

The equipment setup and the experiment procedures followed throughout this research were described in Chapter Two. The general operating parameters for analyzing facilities were tabulated as well.
The oxidation of palladium single crystals was discussed in Chapter Three through Chapter Six. The detailed layout was: Chapter Three: Oxidation of Pd(111) at 600 K in 1-150 Torr O₂. Chapter Four: Oxidation of Pd(110). Chapter Five: Oxidation of Pd(100). And Chapter Six: Oxidation of Pd(111) at high temperature of 780-900 K in 1 Torr O₂.

The surface area increase by treatment in O₂ and in catalytic CH₄ combustion atmosphere was discussed in Chapter Seven.

The catalytic CH₄ combustion over Pd single crystal catalysts was discussed in Chapter Eight. Carbon was found to dissolve in the Pd metal bulk during CH₄ combustion under rich condition but not under lean condition.

Chapter Nine concluded the results in this research. A list for proposed future work was included in Chapter Ten.
REFERENCES


Figure 1.1  Schematic diagram of conventional flame combustion gas turbine system
Figure 1.2  NO\textsubscript{x} formation as a function of temperature
Figure 1.3    Schematic diagram of catalytic combustion gas turbine system
2 Experimental Setup
2.1 Experimental system

The objective of this research is to characterize the surface structure transformations of Pd model catalysts during O$_2$ oxidation and catalytic CH$_4$ combustion. Surface study is commonly carried out in Ultra-High Vacuum (UHV) system to eliminate all potential contaminants. Thus the experiments in this research were mainly performed in a UHV system equipped with three stainless steel chambers pumped by three turbo-molecular pumps and an ion sublimation pump. Figure 2.1 represents the scheme of the UHV system.

The first chamber was a high-pressure reaction/load-lock cell pumped with two 110 L s$^{-1}$ turbo-molecular pumps. The pressure in this chamber could be well controlled in the range of $10^{-6}$-1000 Torr (1 Torr = 133.3 Pa). Palladium single crystals and STM scanning tips were loaded into the UHV system from this cell, and then transferred to the other two chambers by means of a 142 cm rotatable magnetic transfer arm (MDC Vacuum Products Corp.). Oxidation of Pd single crystals in O$_2$ pressure 1-150 Torr was also performed in this cell at elevated temperatures (600-900 K). The sample was heated by an infrared spotlight (Research Inc.) from outside the cell. Sample temperature was measured by a chromel-alumel thermocouple spot-welded on the side of the single crystals and controlled by a Eurotherm 2408 temperature controller (Eurotherm Controls Inc.) interfaced with a silicon controlled rectifier (SCR Eurotherm Controls Inc.). A sapphire view port window (MDC Vacuum Products Corp.) was chosen to allow the infrared beam to focus on the sample, since sapphire has the least infrared light screening effect and a low thermo expansion coefficient, thus preventing to be overheated and broken. Ultra-pure (99.998%, Matheson Tri-gas Inc.) oxygen gas was introduced from a
leak valve to provide precise pressure control. Nitrogen (News Inc. 99.8%) was inlet from manifold valve when atmospheric pressure was required. Besides, the H₂ reduction of pre-oxidized Pd single crystals, the ¹⁸O isotope exchange and the catalytic CH₄ combustion reactions were carried in this high-pressure reaction cell as well.

The second chamber, operating under UHV condition, accommodated an ambient-temperature UHV Scanning Tunneling Microscopy (STM, STM100, RHK Inc.). This STM chamber was pumped by a 270 L s⁻¹ turbo molecular pump to maintain a base pressure after baking out in the range of 1 × 10⁻⁹ Torr. Besides an STM scanning head (including all the electronics and a scanning tip), this chamber was equipped with a copper sample stage, a copper tip conditioning stage and a storage fork arm to temporarily store samples and spare scanning tips. In order to minimize all the possible vibrations, the STM chamber was supported on four air-legs (Newport Corp.) and floated during scanning. The whole electronics were well grounded through copper wires to reduce electrical noise.

The third chamber in this experimental UHV system was an analysis chamber housing instrument facility for surface science study. This chamber included: (1) a Mass Spectrometer (MS, RGA-200, Stanford Research Systems, Inc.) for Temperature Programmed Desorption and Temperature Programmed Decomposition (TPD); (2) a Low Energy Electron Diffraction (LEED, OCI Inc.) for the study of crystal structure; (3) an electronic gun with a Double Pass Cylindrical Mirror Analyzer (CDMA, PHI 15-255G, Physical Electronics Inc.) for Auger Electron Spectroscopy (AES) to determine the surface composition and for X-ray Photoelectron Spectroscopy (XPS) to determine the surface chemical states; and (4) an Ar⁺ ion sputtering gun (PHI 04-161, Physical
Electronics Inc.) to clean the surface of palladium samples. Pd catalyst samples could be moved in three dimensions and rotated to face all analyzing instruments using a manipulator (Vacuum Generators Inc.). Pd single crystal was mounted on commercial variant temperature RHK sample holder (RHK Inc.) for both STM scanning and sample treatments. In this chamber the sample was heated via a custom-designed electron beam bombardment gun from the rear and the temperature was controlled by a Eurotherm 2408 controller interfaced with a custom-designed DC power supply. Ultra-pure oxidant gases, O$_2$ and NO$_2$ were fed into this chamber through two variable leak valves and guided by a copper doser to the sample for cleaning, oxidation or adsorption study purposes. Other pure gases, for example, Ar (99.9999%, Matheson Tri-gas Inc.) and N$_2$ (99.9999%, Matheson Tri-gas Inc.) were inlet into the chamber through separate leak valves. This chamber was pumped with a powerful ion sublimation pump to reach a $5 \times 10^{-10}$ Torr base pressure.

### 2.2 Experimental procedure

#### 2.2.1 Sample cleaning

Single crystal Pd(111) (diameter 7.2 mm × thickness 0.8 mm, mis-orientation < 0.5°, Princeton Scientific Corp.) was cleaned in the analysis chamber by repeating cycles of Ar$^+$ ion sputtering (sputtering with 0.5-2 keV Ar$^+$ ion at sample temperature of 900 K or room temperature for 5 min), annealing (1100 K for 60 s), O$_2$ or NO$_2$ exposure (O$_2$ pressure of $5 \times 10^{-7}$ Torr at sample temperature 850 K for 15 min without doser, or O$_2$ pressure of $5 \times 10^{-8}$ Torr at sample temperature 570 K for 10 min with doser, or NO$_2$ pressure of $2 \times 10^{-8}$ Torr at sample temperature 510 K for 10 min with doser, doser effect
was estimated to be about 60 times, see section 2.2.3), and flashing (1100 K for 60 s), until no impurity peaks were detected by AES. Since the KLL signal of carbon overlaps the MNN signal of palladium, it was difficult to detect trace amount of carbon by AES. Instead, \( \text{O}_2 \) titration was used to determine whether the sample surface was free of carbon until no appearance of CO or \( \text{CO}_2 \) desorption peaks in TPD pattern was observed.

Single crystal Pd(100) and Pd(110) (both with diameter 8.5 mm \( \times \) thickness 1.0 mm, misorientation < 0.5°, Princeton Scientific Corp.) were cleaned in a similar matter as that for Pd(111), except that lower flashing and annealing temperatures around 1000 K were employed.

### 2.2.2 Calibration of doser effect

For oxygen adsorption experiments in the analysis chamber, a copper tube doser (1/16” in diameter) guided both oxidant gases, \( \text{O}_2 \) and \( \text{NO}_2 \) from each leak valve to the Pd single crystal sample surface. The sample was positioned about 3 mm from the end of the tube, leading to a high effective pressure at the sample surface compared with the background pressure. The doser effect was calibrated by comparing the exposure required to achieve certain oxygen coverage, determined from the integration of TPD peak area, when the sample was located in front of the doser tube, with when the sample was turned away from the tube and a by-pass loop was open. An estimated 60 times of doser effect was thereafter determined by exposure of Pd(111) to \( \text{NO}_2 \) in the range of 1-10 Langmuirs (L).
2.2.3 Calibration of exposure

Exposure of Pd single crystal sample to oxidant gases in front of the thin copper tube doser resulted in continuously increasing background pressure in the analysis chamber until after a significant amount of time to reach final equilibrium. This effect could introduce non-negligible errors in the calculation of exposure if one simply multiplied pressure by exposing time. In order to precisely determine exposure, a Labview program was designed to monitor pressure (read from ion-gauge controller) vs. time using a model PCI-MIO-16XE-50 acquisition card (National Instruments, Inc.). Exposure was thereafter obtained by integrating the pressure-time area.

2.2.4 Calibration of oxygen coverage

2.2.4.1 Oxygen coverage on Pd(111)

At room temperature (RT) the oxygen coverage on Pd(111) single crystal saturated after exposure to 10-30 L of pure oxygen. A p(2×2) adsorbate structure was observed by both LEED and STM indicating a 0.25 monolayer (ML) saturation coverage [1, 2]. The oxygen coverage could be increased beyond the 0.25 ML by exposing the surface to a stronger oxidant for example NO₂ [2, 3], and a 2.4 ML oxygen saturation coverage was observed after about 50 L NO₂ exposure at 500 K [2]. In this research, since relatively high uptakes were measured, we used the TPD peak integral following saturation NO₂ doses at 500 K to calibrate the oxygen coverage on Pd(111).
2.2.4.2 Oxygen coverage on Pd(100)

Oxygen dissociative adsorption on Pd(100) induced four surface structures as observed with LEED and STM at increased oxygen coverages including p(2×2), c(2×2), (5×5) and (\(\sqrt{5} \times \sqrt{5}\))R27° [4-9]. The p(2×2) LEED pattern is observed for coverages ranging from 0.05 ML to 0.25 ML, which is gradually replaced by c(2×2) upon increasing oxygen exposure with maximum coverage of 0.5 ML. The two reconstructed structures (5×5) and (\(\sqrt{5} \times \sqrt{5}\))R27° have ideal coverages of 0.64 ML and 0.80 ML [6, 10]. In this research, the saturated 0.8 ML uptake with a (\(\sqrt{5} \times \sqrt{5}\))R27° structure obtained by O₂ exposure at 550 K was used as the calibration of oxygen coverage on Pd(100).

2.2.4.3 Oxygen coverage on Pd(110)

A variety of ordered structures formed by oxygen adsorbed on Pd(110) have been reported in the literature. These ordered structures included (1×3), (1×2), c(2×4), and c(2×6) to some even complex structures, depending on the oxygen coverage and temperature [11-22]. General agreement however has been reached that upon oxygen exposure at elevated temperature around 400 K, a relatively stable surface reconstruction c(2×4) phase was formed with saturated 0.5 \(\pm\) 0.05 ML oxygen coverage [13, 14]. In this research the oxygen coverage on Pd(110) was calibrated with the TPD integral peak area obtained on the c(2×4) phase checked with LEED after about 12 L O₂ exposure at 570 K.
2.2.5 Oxidation of Pd single crystals in O₂

The following experimental protocol was used for oxidation experiments. The single crystal was heated to the desired temperature in vacuum and then oxygen was introduced. After oxidation, the sample was cooled and oxygen was pumped out simultaneously. It took less than 1 min to reduce the sample temperature to 450 K and to reach the vacuum in the reactor better than 10⁻⁶ Torr.

2.2.6 H₂ reduction of pre-oxidized Pd sample

H₂ reduction experiments were performed in the high-pressure reaction cell. The single crystal was pre-oxidized for 30 min in 150 Torr of O₂ at 600 K and then cooled to RT before oxygen was pumped out. The oxidized sample was heated to the desired reduction temperature at a pressure in the reaction chamber better than 10⁻⁷ Torr and then 1 Torr of H₂ was introduced for 1 min. The H₂ was evacuated at a pressure better than 10⁻⁶ Torr before the reduced sample was cooled to RT.

2.2.7 ¹⁸O isotope change

The ¹⁸O isotope exchange experiment was carried out following the procedure described by Moteiro et al. [23]. Briefly an oxidized palladium sample was exposed to 5 Torr ¹⁸O₂ (>99%, Isotec Inc.) at 600 K for 12 s, and the uptake of ¹⁸O exchanged was then measured by TPD analyzing all gases containing labeled oxygen.
2.2.8 Catalytic CH₄ combustion

The combustion of methane on Pd single crystals was performed in the high-pressure reaction cell 615 cm³ in volume in a batch mode. The reaction gases were introduced from a gas manifold in the following order: N₂ (624 Torr), O₂ (160 Torr) and CH₄ (16 Torr)(99.999%, Matheson Tri-gas Inc.) for oxidation in lean condition or N₂ (624 Torr), CH₄ (160 Torr) and O₂ (16 Torr) for oxidation in rich condition. The reactants were mixed for 30 min before reaction by a circulation pump model MB-21 (Metal Bellows, Inc.) at a nominal rate of 1000 cm³ min⁻¹. Reaction was normally carried out at 600 K for 60 min with about 2.5% of the CH₄ being consumed for oxidation in lean condition and about 3% for oxidation in rich condition. The reaction mixture was analyzed with an Agilent 6890 Series gas chromatograph (GC) using a thermal conductivity detector, and a 15-ft Carboxen 1000, 60/80 mesh column.

2.3 Preparation of STM tips

The quality of STM tips is an important factor that affects the resolution of the STM images. The art to prepare sharp tips from metal wires of tungsten (W) and platinum-iridium (Pt 90%/Ir 10%) has been developed in the literature. Two common ways of fabricating tips are cutting the wire with a wire cutter and drop-off electrochemical etching [24, 25].

Cutting tips is applicable only when flat surfaces are characterized because the resulting tip surface is actually quite jagged. The jagged surface of a cut tip has a number of very small individual protrusions one of which may act as a well-defined minitip. It was
suggested that there might be one atom at the apex of such a minitip that forms a stable point of tunneling on almost planar surfaces [25].

In many cases when a rough surface is to be studied over a large scanning range, for example during investigation of the Pd surface after high-pressure O\textsubscript{2} treatment as in this research, the surface is drastically roughened and the sharpness and geometry of the tip becomes crucial. Electrochemically etched tips are especially used to meet this crucial requirement. The basic idea of electrochemical etching is that when the lower part of the etched wire drops off, the etching current through the tip is cut off as soon as possible to prevent it from blunting the tip [26].

2.3.1 Preparation of W tip

The corresponding electrochemical etching reactions for W tip preparation involve the anodic dissolution of tungsten in aqueous base and water electrolysis at the cathode [26]:

\[
\begin{align*}
\text{Cathode} & : \quad 6H_2O + 6e^- \rightarrow 3H_2(g) + 6OH^- \quad SRP = -2.48V \\
\text{Anode} & : \quad W(s) + 8OH^- \rightarrow WO_4^{2-} + 4H_2O + 6e^- \quad SOP = +1.05V \\
\text{Total} & : \quad W(s) + 2OH^- + 2H_2O \rightarrow WO_4^{2-} + 3H_2(g) \quad E^0 = -1.43V
\end{align*}
\]

Figure 2.2 illustrates the setup for electrical W tip etching used in this research. At the anode, tungsten was oxidative dissolved to be soluble tungstate (WO\textsubscript{4}\textsuperscript{2-}) anions. And at the cathode, water was reduced to release bubbles of H\textsubscript{2} and OH\textsuperscript{-} ions. Tungstate was formed once the applied potential exceeded the standard electrode potential \((E^0)\) 1.43 V. Typically, with our experimental setup, tungsten wire used to make tip was 10 mil (0.25
mm) in diameter and dipped into a 2 mol L\(^{-1}\) KOH aqueous solution. The applied AC voltage was around 1.8 V. Current passing through was in the range of 10-15 mA. Etched tip was rinsed in deionized water followed by ethanol cleaning. The sharpness of the etched W tip was studied by SEM. Although the W tip appeared to be sharp, it did not always have a stable performance while scanning. The reason could be due to that the W tip was vulnerable to be oxidized or due to some variability in the etching process.

### 2.3.2 Preparation of Pt-Ir tip

High quality STM tip is always made from Pt-Ir. The electrochemical reactions for Pt-Ir tip etching include the attachment of chloride ions Cl\(^{-}\) to the platinum anode followed by detachment of the complexes PtCl\(_4\)\(^{2-}\) or PtCl\(_6\)\(^{2-}\) [25, 27]. Figure 2.3 shows a schematic of the setup for preparation of Pt-Ir tip. Pt (90%) –Ir (10%) wire 10 mil in diameter was dipped into a salt mixture molten solution. The salt was a mixture by NaNO\(_3\) and NaCl 4:1 in molar ratio. Temperature to melt the salt mixture was controlled at around 400-450 °C and 2 V DC was applied between anode and cathode to achieve around 10 mA current passing the electrochemical cell.

### 2.4 Guideline for instrument operating conditions

The UHV system used in this research was equipped with a MS, AES, LEED and STM to characterize the surface changes both morphology and chemical composition on Pd single crystals during high-pressure O\(_2\) treatment and catalytic CH\(_4\) combustion. MS was used to track the oxygen desorption from the Pd catalyst. AES gave information on the surface chemical composition present in the surface layers of the sample. LEED was used to determine the surface lattice structure of single crystals. And the surface
morphology transformation during O$_2$ exposure was investigated by STM. The operating conditions employed in this research for each instrument are listed in Table 2.1-2.4. The operating conditions for Ar$^+$ ion sputtering gun (Table 2.5) are also included in this section for future reference.
REFERENCES


**Table 2.1**  MS operating conditions

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Mass spectrometer</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Operating conditions</strong></td>
<td></td>
</tr>
<tr>
<td>Emission current:</td>
<td><strong>1.00 mA</strong></td>
</tr>
<tr>
<td>HV bias on CDEM:</td>
<td><strong>1100 V</strong></td>
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<td>Noise Floor:</td>
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<td>Single mass measurement time:</td>
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### Table 2.2  AES operating conditions

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Auger Electron Spectroscopy</th>
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</thead>
<tbody>
<tr>
<td><strong>Operating conditions</strong></td>
<td></td>
</tr>
<tr>
<td>Beam energy: 2 keV</td>
<td></td>
</tr>
<tr>
<td>Emission current: 2 mA</td>
<td></td>
</tr>
<tr>
<td>Beam current: 1-3 µA</td>
<td></td>
</tr>
<tr>
<td>Instrument</td>
<td>Low Energy Electron Diffraction</td>
</tr>
<tr>
<td>------------</td>
<td>--------------------------------</td>
</tr>
<tr>
<td><strong>Operating conditions</strong></td>
<td>Filament current: <strong>2.8 A</strong></td>
</tr>
<tr>
<td></td>
<td>Beam voltage: <strong>40-200 eV</strong></td>
</tr>
<tr>
<td></td>
<td>Beam current: <strong>1-3 μA</strong></td>
</tr>
<tr>
<td></td>
<td>Focus voltage: <strong>50-200 V</strong></td>
</tr>
<tr>
<td></td>
<td>Screen voltage: <strong>4.00 kV</strong></td>
</tr>
<tr>
<td></td>
<td>Retarding voltage: <strong>50-100% of the beam voltage</strong></td>
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</table>
**Table 2.4**  STM operating conditions

<table>
<thead>
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<th>Instrument</th>
<th>Scanning Tunneling Microscopy</th>
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<tbody>
<tr>
<td><strong>Operating conditions</strong></td>
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<tr>
<td>Tunneling current:</td>
<td>0.1-2 nA</td>
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<tr>
<td>Bias voltage:</td>
<td>± 0.1-4 V</td>
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<tr>
<td>Gain:</td>
<td>5-8</td>
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<tr>
<td>Time constant:</td>
<td>2-4</td>
</tr>
<tr>
<td>Instrument</td>
<td>Ar⁺ sputtering gun</td>
</tr>
<tr>
<td>---------------</td>
<td>--------------------</td>
</tr>
<tr>
<td><strong>Operating conditions</strong></td>
<td>Ar pressure: $5 \times 10^{-5}$ Torr</td>
</tr>
<tr>
<td></td>
<td>Beam voltage: 0.5-2.0 keV</td>
</tr>
<tr>
<td></td>
<td>Filament current: 20 mA</td>
</tr>
</tbody>
</table>
FP1: Mechanical pump 1  
TP1: Turbo pump 1 270 L s⁻¹  
FP2: Mechanical pump 2  
TP2: Turbo pump 2 110 L s⁻¹  
FP3: Mechanical pump 3  
TP3: Turbo pump 3 110 L s⁻¹  
AP1: Absorption pump 1  
AP2: Absorption pump 2  
TG1: Thermocouple gauge 1  
IG1: Ion gauge 1  
TG2: Thermocouple gauge 2  
IG2: Ion gauge 2  
TG3: Thermocouple gauge 3  
IG3: Ion gauge 3  
IP: Ion pump

**Figure 2.1** Equipment scheme
Figure 2.2  Experimental setup for W tip etching
Figure 2.3  Experimental setup for Pt-Ir tip etching
Chapter

3 High Pressure Interaction Between Pd(111) and \( \text{O}_2 \): Oxidation or Dissolution?
Abstract

The interaction between Pd(111) and O₂ in the pressure range of 1-150 Torr was studied by Temperature Programmed Desorption (TPD), Auger Electron Spectroscopy (AES), Low Energy Electron Diffraction (LEED) and Scanning Tunneling Microscopy (STM). The diffusion of oxygen atoms into palladium near surface region was found to compete with the oxidation at 600 K. The dissolution of oxygen was a diffusion-limited process. The activation energy for the oxygen diffusion was equal to 84 kJ mol⁻¹. The oxygen dissolution resulted in the maximum 14% outward expansion of the inter-planar spacing for the first two surface layers after an exposure to 25 Torr O₂ at 600 K for 10 min. Oxide phase appeared when a critical concentration of oxygen was reached in the near-surface region. Nucleation of the oxide phase started in the vicinity of the steps. The oxidized Pd(111) surface exhibited a “cauliflower-like” structure composed of semi-spherical agglomerates 1.5-4.0 nm in size, with an surface area increase of 87% after an exposure to 100 Torr O₂ at 600 K for 10 min. The dissolved oxygen stabilized the oxide phase, and therefore oxide layer decomposed at higher temperatures around 775 K, comparing to the 610 K after NO₂ exposure.
3.1 Introduction

Catalytic combustion of methane is an environmentally friendly alternative to conventional combustion in gas-fired turbines because it can reduce thermally generated NO\textsubscript{x} emissions [1]. Palladium is the most active metal for methane combustion [2]. And recently Pd catalytic combustors appeared for commercial applications [3]. In order to improve catalyst performance, a number of fundamental questions should be answered. Since the real catalytic reaction is operated in the conditions when either palladium oxide or palladium metal is a thermodynamically stable phase, oxygen interaction with palladium is of particular interest.

There are a number of publications in the literature devoted to the interaction of Pd single crystal surfaces with oxygen at low pressures typically below 10\textsuperscript{-6} Torr (1 Torr = 133.3 Pa), see for instance [4-22] and the references therein. At room temperature (RT) on a Pd(111) surface, oxygen adsorbs dissociatively and forms a p(2\times2) adlayer with a saturated coverage of 0.25 monolayer (ML, 1 ML = 1.53 \times 10\textsuperscript{15} atoms cm\textsuperscript{-2}) [8, 21]. A higher oxygen uptake beyond the surface saturation coverage could be reached either by O\textsubscript{2} treatment under high pressure and/or temperature [11, 13, 18] or by dosing a stronger oxidant such as NO\textsubscript{2} [4, 21]. After exposure of a Pd(111) surface to NO\textsubscript{2}, the coverage could reach 2.4 ML [21]. An incommensurate two-dimensional surface oxide could be formed, which was characterized by its unique lattice structure detected using Scanning Tunneling Microscopy (STM) [13, 21] and Low Energy Electron Diffraction (LEED) [18, 21]. A number of islands and peninsulas were observable as well [21]. The similar surface oxide layer was formed by exposure to O\textsubscript{2} in different conditions [11, 13, 18].
The oxygen coverage assigned to the 2D surface oxide ranged from 0.67 ML [13] and 1 ML [11] to 1.5-1.8 ML [21]. Removal of this surface oxide layer by reduction in CO [11] or annealing in high vacuum at 623 K [13] resulted in the formation of hexagonal 1 ML deep holes. The low Pd surface atom density in the hole-structure (around 30% lower than the normal structure) was then suggested to correspond to the low Pd density in the surface oxide [11]. The diffusion of oxygen into the palladium subsurface region starts at elevated temperature above 523 K [6, 12].

Despite the enormous amount of research on O/Pd interaction in low pressure, the palladium oxidation under realistic conditions, which is of interest for the industrial application, has not been well investigated. Thus, in this work we focused on the interaction between a Pd(111) surface and O₂ in the pressure range of 1-150 Torr. The oxidation mechanism for Pd(111) in high-pressure O₂ and the surface morphology transformation from Pd metal to Pd oxide were investigated.

3.2 Experimental Methods

The experiments were carried out in a specially designed system consisting of three stainless steel chambers: an Ultra-High Vacuum (UHV) analysis chamber, a UHV STM chamber and a high-pressure reaction cell. The analysis chamber housed facilities for Auger Electron Spectroscopy (AES), Temperature Programmed Decomposition (TPD), LEED and STM. The STM chamber accommodated an ambient-temperature UHV STM (RHK Inc.). The base pressure in UHV chambers after bake out was $5 \times 10^{-10}$ Torr and in the high-pressure reaction cell was $2 \times 10^{-8}$ Torr.
The sample was a 0.8 mm thick, 7.2 mm diameter single crystal of Pd(111) (Princeton Scientific Corp.) with mis-alignment < 0.5°. The single crystal was mounted on a standard RHK sample holder. The temperature was measured by a chromel-alumel thermocouple spot-welded onto the side of the sample. In the analysis chamber, the sample was heated by electron-bombardment from the rear. In the reaction cell, the sample was heated using an IR lamp.

The TPD spectra were collected by means of a RGA-200 Mass Spectrometer (MS) at a constant heating rate of 5 K s⁻¹. The coverage was calculated by integrating area under a TPD peak and measured in ML. Since relatively high uptakes were measured, the maximum coverage of 2.4 ML obtained by exposure to 50 L NO₂ at 500 K was used for calibration [21].

The sample cleaning procedure consisted of repeating cycles of Ar⁺ sputtering at room and elevated temperatures, annealing up to 1100 K, exposure to O₂ and/or NO₂ followed by flashing at 1100 K for 60 seconds under UHV conditions. The sample cleanliness was checked by TPD, AES and LEED. NO₂ and O₂ were introduced into the analysis chamber through a capillary dozer.

STM images were obtained using Pt-Ir tips electro-chemically etched in NaCl/NaNO₃ melt at around 400-450 °C. The surface area was measured from STM images by taking discrete image pixels and joining them by a series of triangles. Integration of the area of individual triangle gives the total area [23].

Treatments in 1-150 Torr O₂ were performed in the high-pressure reaction cell. The following treatment protocol was used. The single crystal was heated up to the desired
temperature in vacuum and oxygen was then introduced. After O\textsubscript{2} exposure, the sample was cooled down and oxygen was pumped out simultaneously. It took less than 1 min to cool the sample to 450 K and to reach the vacuum in the reaction chamber better than 10\textsuperscript{-6} Torr. After a treatment, the sample was transferred into the STM and/or analysis chamber by means of a 142 cm transfer arm without contact with atmosphere.

3.3 Results

3.3.1 Temperature programmed desorption

Figure 3.1 represents the oxygen TPD traces obtained after exposure of the Pd(111) single crystal to 1-150 Torr O\textsubscript{2} at 600 K for 10 min. The oxygen uptake as a function of O\textsubscript{2} pressure is shown in Figure 3.2. TPD spectrum obtained after exposure of the Pd(111) to 50 L NO\textsubscript{2} at 500 K is also shown in the bottom of Figure 3.1 for comparison. The NO\textsubscript{2} dosing resulted in a narrow and symmetric oxygen desorption peak at 740 K with Full Width at Half Maximum (FWHM) of 22 K. Shoulder peak was distinguishable at lower temperature around 610 K. This TPD spectrum was very similar to those reported in References [4, 21]. The TPD feature at 610 K was assigned to the decomposition of palladium oxide [13]. TPD characteristics observed after 1-150 Torr O\textsubscript{2} treatment were different. Exposure to 1 Torr of O\textsubscript{2} resulted in an asymmetric TPD peak centered at 795 K with FWHM of 50 K. As the oxygen pressure increases, the structure of TPD peaks became more complex. The peak maximum shifted towards higher temperatures and reached 805 K at 25 Torr. After 50 Torr treatment the TPD peak at 805 K transformed to the shoulder of a new peak centered at 795 K. Also a low temperature broad peak at 775 K was well distinguished. This peak grew and dominated after 100
Torr. The complex structure of TPD traces pointed to the fact that a number of various oxygen species formed during high pressure O\textsubscript{2} exposure. Based on the STM data discussed below, the TPD peak at 775 K could be assigned to the decomposition of stoichiometric PdO.

The oxygen uptake increases quickly with O\textsubscript{2} pressure up to 50 Torr and then levels off as shown in Figure 3.2. An equivalent of 18 ML of oxygen desorbed from the Pd(111) surface after exposure to 150 Torr of O\textsubscript{2}. The saturation of the uptake rate could be either diffusion limited or due to inhibition of dissociative adsorption of oxygen by oxide. The O\textsubscript{2} uptake was measured after exposure of the Pd(111) single crystal to 10 Torr of O\textsubscript{2} at 600 K for various treatment time. The oxygen uptake is linearly proportional to the square root of the exposure time as shown in Figure 3.3. This suggested that the uptake was indeed diffusion controlled and conformed to the Mott-Cabrera parabolic diffusion law [24]:

\[ N_{\text{oxygen}} = K \cdot t^{1/2}. \]  

(1)

Here \( N_{\text{oxygen}} \) is the oxygen uptake in ML equivalent and \( K \) is the parabolic rate constant, which is a function of the treatment temperature and the diffusion activation energy.

The activation energy is calculated from an Arrhenius plot of the oxygen uptake versus \( T^{-1} \) as shown in Figure 3.4. The diffusion activation energy of 84 kJ mol\textsuperscript{-1} agreed reasonably well with the literature data [6, 25, 26] summarized in Table 3.1.
3.3.2 Scanning tunneling microscopy

Surface morphology of the Pd(111) treated in various oxygen pressure from 1 to 100 Torr was monitored by STM. The results are shown in Figure 3.5. A number of different features compared to the clean Pd(111) surface were noticed after the exposure to 1 Torr O₂ at 600 K for 10 min. First, small clusters with mean size of 6 Å nucleated and grew on the surface as shown in Figure 3.5(a). The mean distance between the clusters was measured to be 5 Å and the z corrugation was 1.3 Å. Second, the step height was measured to be 2.45 ± 0.1 Å. This value was bigger than that on a clean Pd(111) surface of 2.25 ± 0.05 Å. Third, a number of holes with the mean size of 3 nm and the depth of 2.4 ± 0.1 Å appeared. The holes covered about 30% of the Pd(111) surface. This surface morphology was quite similar to those reported in literatures [11, 13]. Hexagonal 1 ML deep holes were observed after a 2D surface oxide on Pd(111) reduced in 25 L CO at 573 K [11]. Besides the holes, there were a few islands 3 nm in size, expelled from the terraces. The island height was same as the one for the steps and the holes and equal to 2.45 ± 0.1 Å, independent of the sample bias. Finally, the terraces, which were approximately 300-400 Å in width, narrowed up to 100-150 Å after the 1 Torr oxygen treatment. A slightly diffused (1×1) LEED pattern observed after the treatment; moreover AES did not detect any oxygen trace despite the oxygen uptake of 7 ML (Figure 3.2). Current versus voltage function measured using STM (also referred to IV spectroscopy) did not detect the existence of an energy gap. For the sake of truth, we should mention that we were not able to get the image like shown in Figure 3.5(a) everywhere on the surface.
The number of the holes increases after exposure of the Pd(111) crystal to 10 Torr O₂ as shown in Figure 3.5(b). The holes lost their original hexagonal or square shape and elongated in the directions either parallel or perpendicular to the steps. Some holes looked as if they were attached to another one. The depth of the holes and the step height remained unchanged as after 1 Torr treatment, but the step edges became curved, no longer straight as on the clean Pd(111) surface. Differing to the structure obtained after 1 Torr treatment, the surface after the exposure to 10 Torr O₂ was imaged to present an agglomerate feature composed of elongated clusters. Although the shape of the clusters was not quite clear, the general orientation being slightly angled to the steps was visible. The surface area measured from the STM images does not show significant increase after this treatment as shown in Figure 3.6. Again, oxygen was not detected by AES. LEED revealed a diffused Pd(111) (1×1) pattern.

From the first glance the surface does not undergo structural changes after 25 Torr oxygen treatment, compared to that after 10 Torr O₂ exposure as shown in Figure 3.5(c)-(d). However, no metallic Pd(111) spots were observed with LEED except for the bright background. AES detected oxygen with O/Pd atomic ratio of 8.2%. The energy gap of 1.5-2.0 eV was determined by IV spectroscopy on the terrace region. The irregular shape of the holes was likely due to the coalescence of a few nearby holes. The steps were heavily bent and curved like “Norwegian fjord coast”. The step height was increased more to be 2.6 ± 0.1 Å. The elongated clusters appeared after 10 Torr exposure was rounded into a number of semi-spherical agglomerates after the 25 Torr O₂ treatment. Likely these agglomerates were growing stoichiometric oxide phase.
The growth of the oxide layer continues after exposure of the Pd(111) to 50 Torr and 100 Torr of O₂ as shown in Figure 3.5(e)-(h). Atomic step could barely be seen after 50 Torr treatment and became indistinguishable after 100 Torr exposure. The growing PdO formed a number of semi-spherical agglomerates. And these agglomerates tended to aggregate together to form a large “cauliflower-like” superstructure. This tendency of aggregation was more apparent on the surface after 100 Torr treatment. The size of the semi-spherical agglomerates changed slightly with the pressures, being 1.5-2.0 nm and 2.5-4.0 nm at 50 and 100 Torr, respectively. The density of the semi-spherical agglomerates was higher in the vicinity of the atomic steps. Likely, the “cauliflower-like” structure started from the steps. According to AES, the atomic ratio between O and Pd was 21% and 39% after 50 and 100 torr of O₂. The energy gap was in the range of 3.5-4.0 eV. This value was close to the 4.0-5.0 eV energy gap reported for bulk PdO [27].

As expected, the surface area increases drastically as shown in Figure 3.6. An 87% area increase was determined on the surface after an exposure to 100 Torr O₂ at 600 K for 10 min.

The “cauliflower-like” structure could also be formed at low oxygen pressure by extending the O₂ exposure time as shown in Figure 3.7. The sample was prepared by oxidation in 10 Torr O₂ at 600 K for 60 min. Atomic step was not detectable on this surface. The surface area increase of around 42% was comparable with obtained after 50 Torr treatment for 10 min.

The change of the oxygen treatment protocol described in experimental section allowed the observation of another interesting phenomenon. Just reminding that the regular O₂ treatment procedure was to cool the sample after the exposure and to pump out O₂.
*simultaneously*. Whereas, A complex LEED pattern was observed after exposure to 10 Torr O₂ for 10 min at 600 K followed by cooling the sample in oxygen pressure to about 400 K in 1 min before transferring to analysis chamber. This LEED observation was identical to that of a 2D surface oxide [18, 21]. It has been suggested that this oxide structure could be “frozen in” by cooling in O₂ pressure [18].

### 3.4 Discussion

This paper addressed the interaction between palladium and oxygen under pressure close to the real catalytic CH₄ combustion conditions. The thermodynamic equilibrium of the reaction at 600 K in oxygen pressure above 1 Torr is well shifted towards oxide formation.

\[
Pd + O_2 \rightarrow PdO
\]

Therefore it was surprising to find no evidence of oxidation up to 10 Torr oxygen treatment. From the experimental results described above, one can conclude that there occur two competing processes during the oxygen treatment: the diffusion of oxygen atoms into the Pd metal and the formation of Pd oxide. The diffusion plays the leading role at low oxygen pressure whereas the oxidation starts to dominate at pressure above 10 Torr.

#### 3.4.1 Oxygen diffusion

At low coverage below 0.25 ML on the Pd(111) surface, i.e. before a p(2×2) oxygen adlayer formed, the dissociative sticking probability of oxygen is high and thereby masks the slow diffusion into the bulk. The migration of oxygen into palladium, however
becomes energetically feasible when the oxygen uptake increases beyond the surface saturation coverage as a consequence of the reduced oxygen binding energy. This diffusion process involves a temperature-activated step. Thus, the penetration of oxygen atoms into the subsurface region occurred at a temperature above 523 K was suggested by Leisenberger et al. [12]. The subsurface reservoir would be populated by high pressure oxygen dosing at elevated temperatures for example 8,000 L at 1000 K [12, 28]. After exposing a Pd polycrystalline foil at 1023 K in 10^{-2} Torr O_2, an equivalent of 350 ML oxygen was detected to incorporate into the Pd bulk without the formation of PdO [6]. However, sake of truth it should be noted that oxide is not thermodynamically favorable phase at this treatment conditions [6]. This temperature-activated oxygen dissolution process also occurred during the high-pressure O_2 treatment as shown in the present work. The activation energy is estimated to be 84 kJ mol^{-1} (Figure 3.4). Since the oxygen uptake is linearly proportional to the square root of the treatment (Figure 3.3), the oxygen dissolution should be diffusion limited at least up to O_2 pressure of 10 Torr. Dissociative adsorption of oxygen is unlikely to rate determining step in these conditions.

A number of oxygen species can form on Pd(111) depending on the Pd-O interaction. These species include the dissociatively adsorbed oxygen which forms a p(2\times2) pattern and desorbs at approximately 800 K [8, 21]; the 2D surface oxide that represents a complex LEED pattern and decomposes in vacuum at approximately 740 K; and the oxygen species that strongly bounds to the Pd atoms and desorbs at above 1070 K [12, 29]. This oxygen species used to be referred as subsurface oxygen [12, 28] or the bulk oxygen [8]. The difference between the three oxygen species is further revealed by their different reactivity towards CO. Both the chemisorbed oxygen and the 2D surface oxide
react with CO [11, 12]; whereas the strongly bounded oxygen species is non-active [8, 12, 30, 31]. In this paper we report another oxygen species, which is the oxygen dissolved in the near surface region. The Pd(111) surface containing this oxygen species demonstrates a slightly diffused Pd(111) (1×1) LEED pattern. The near surface oxygen causes an expansion of the Pd lattice: the monatomic step increases by 9%-14% after 1-25 Torr O$_2$ treatment.

Comparing to the oxygen species strongly bounded to Pd atoms, the species in the near surface region has lower thermo-stability. It desorbs at 795-805 K (Figure 3.1), lower than the desorption temperature for the strongly bounded species (over 1070 K) but slightly high than the dissociation of 2D surface oxide (around 740 K). The surface adsorbed oxygen and the oxygen dissolved in the near surface region demonstrate similar desorption temperatures. This could be due to that desorption of the species dissolved in the near surface region are in the equilibrium with the adsorbed oxygen. The desorption of surface adsorbed oxygen is the rate-determining step of the process.

To differentiate the oxygen species in the near surface region with the strongly bounded oxygen, we will refer the latter species as bulk oxygen (not subsurface oxygen) throughout this research.

3.4.2 Palladium oxidation

The dissolved oxygen species in the near surface region is supposed to be a precursor for the bulk oxide. The concentration of oxygen increases as the oxygen atoms diffuse into Pd metal continuously. At a certain critical concentration, a new oxide phase nucleates and grows. The critical concentration can be achieved depending on (i) O$_2$ pressure, (ii)
treatment time and (iii) temperature. Thus, the oxide phase was observed after the treatments in O₂ above 50 Torr for 10 min (Figure 3.5(e)-(f)) or in 10 Torr O₂ but for prolonged exposure time above 60 min (Figure 3.7).

The bulk oxide phase appears to have a “cauliflower-like” surface structure composed of semi-spherical agglomerates (Figure 3.5(e)-(h) and 3.7). The density of the “cauliflower-like” structure is higher in the vicinity of the steps when the bulk PdO starts (Figure 3.5(f) and (h)). The orientation of the steps on a fcc(111) surface is (110). Oxidation of a Pd(110) surface suggested that the oxygen diffusion from surface to bulk depends on the surface crystallography, with the highest diffusion rate on the open Pd(110) [29]. Therefore, the critical concentration of the dissolved oxygen can be reached easier in the vicinity of the steps. The oxide nucleation is also expected to start in this region. The surface area increased considerably as the “cauliflower-like” oxide structure formed. The 87% surface area increase after oxidation in 100 Torr O₂ at 600 K for 10 min in respect to a clean Pd(111) surface was in good agreement with the two fold increase on a Pd polycrystalline foil after exposure to a lean methane mixture (16 Torr CH₄, 160 Torr O₂ and 624 Torr N₂, at 600 K) measured by ¹⁸O isotope exchange [32]. The surface area measurement on Pd surface after treatment in various conditions is a subject of another publication [23].

The oxygen uptake levels off after the bulk oxide formed (Figure 3.2). Since oxide has been suggested to enhance the oxygen adsorption [33], the dissociative adsorption is not the rate-limiting step. The only reasonable explanation for the decreasing of the uptake rate is the reduced oxygen diffusion rate in bulk oxide phase, as the oxide is commonly regarded as an oxygen diffusion barrier. An increase in the diffusion rate after the
formation of oxide phase is however occasionally reported. For instance, Outlaw et al. [34] found that slight oxidation of a silver surface could promote the diffusion by roughening the surface and creating structural defects. The bulk PdO surface as shown in Figure 3.5(e)-(h) and Figure 3.7 appears to have a relatively dense structure. It has also been suggested that oxidation of a Pd-film catalyst or a Pd polycrystalline foil in a methane/oxygen mixture with excess O₂ would result in the formation of a dense and smooth Pd oxide layer whereas the porous oxide structure formed in excess of CH₄ [35-37].

The decomposition of bulk PdO in a TPD experiment was found to peak at 775 K (Figure 3.1). A much lower decomposition temperature of around 590 K was however suggested by Zheng and Altman [21] after the exposure to NO₂. We suppose that the oxide phase is stabilized by the dissolved oxygen, and therefore decomposition of the “cauliflower-like” oxide occurs at higher temperatures.

### 3.4.3 2D surface oxide

No two-dimensional surface oxide was detected after 10 Torr treatment at 600 K for 10 min by means of LEED, AES and STM. However, we cannot rule out that the 2D surface oxide forms in these conditions as an intermediate state and then transforms into the dissolved species and/or desorbs upon oxygen evacuation. The LEED pattern of the 2D surface oxide was observed when the Pd(111) surface after a 10 Torr/600 K treatment was cooled in O₂ (see the Result Section). Also the 1 ML holes, which were similar to those observed after the decomposition of surface oxide [11, 13], appeared on the surface after 1 and 10 Torr treatments (Figure 3.5(a) and (b)). Therefore one might conclude that
the 2D oxide being stable during the treatment disappears when the oxygen treatment is quenched.

3.5 Summary

The interaction of oxygen with the surface of a Pd(111) single crystal was studied by STM, LEED, TPD, and AES in a wide pressure range from 1 to 150 Torr at 600 K. The dissolution of the oxygen in the near surface region followed by bulk oxide formation was found. The activation energy of the oxygen diffusion was estimated to be 84 kJ mol$^{-1}$. The oxygen dissolution in the palladium near surface region resulted in the expansion of lattice spacing. After 1 and 10 Torr oxygen treatment, the step height was measured to be $2.45 \pm 0.1 \, \text{Å}$, that was almost 9% higher than the steps on the clean Pd(111) surface. And after 25 Torr treatment, the step height was $2.6 \pm 0.1 \, \text{Å}$, about 14% higher than the theoretical monatomic step height.

The oxide phase occurred when a critical concentration of oxygen was reached in the near-surface region. Since a critical concentration was easier to reach in the vicinity of the step, oxidation started from the steps. The oxide phase exhibited a “cauliflower-like” structure composed of semi-spherical agglomerates. The surface area increased by 87% after oxidation in 100 Torr O$_2$ at 600 K for 10 min. Extension of the O$_2$ exposure time also led to the roughening of the Pd surface. The dissolved oxygen stabilized the oxide phase, and therefore oxide layer decomposed at higher temperatures.
REFERENCES


Table 3.1 Comparison of activation energy for oxygen diffusion in Pd

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E^{*}_{\text{diffusion}}$, kJ mol$^{-1}$</th>
<th>Oxygen pressure, temperature</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(110)</td>
<td>84</td>
<td>UHV, 523 K</td>
<td>[25]</td>
</tr>
<tr>
<td>Pd foil</td>
<td>72</td>
<td>$3.5 \times 10^{-2}$ Torr; 1023 K</td>
<td>[6]</td>
</tr>
<tr>
<td>Pd(110)</td>
<td>92</td>
<td>$10^{-2}$-$10^{-3}$ Torr; 350-400 K</td>
<td>[26]</td>
</tr>
<tr>
<td>Pd(111)</td>
<td>84</td>
<td>1 Torr; 600-800 K</td>
<td>Present work</td>
</tr>
</tbody>
</table>
Figure 3.1  TPD spectra obtained after exposure of the Pd(111) to different O$_2$ pressure at 600 K for 10 min. TPD spectrum obtained after 50 L NO$_2$ exposure at 500 K was also shown in the bottom. The heating rate is 5 K s$^{-1}$. 
Figure 3.2 Oxygen uptakes after O$_2$ exposure on Pd(111) at 600 K for 10 min
Figure 3.3  Oxygen uptake measured in ML from the Pd(111) surface exposed to 10 Torr of O\textsubscript{2} at 600 K as a function of O\textsubscript{2} exposure time.
Figure 3.4  The Arrhenius plot of the oxygen uptake from the Pd(111) surface exposed to 1 Torr of O₂ for 10 min. The oxygen uptake is measured in ML. The apparent activation energy is estimated to be 84 kJ mol⁻¹.
Figure 3.5 STM images of the Pd(111) surface after exposure to (a) 1 Torr, (b) 10 Torr, (c)-(d) 25 Torr, (e)-(f) 50 Torr and (g)-(h) 100 Torr of O₂ at 600K for 10min. The sample bias was in the range of 0.1 V and 1 V. The tunnelling current was 0.1-1 nA. Arrows designate the ‘monatomic’ steps.
Figure 3.6  Surface area increase in relation to the clean surface is calculated by STM image analysis of the Pd(111) surface exposed to O$_2$ at 600 K for 10 min.
Figure 3.7  STM image of the Pd(111) surface after exposure to 10 Torr of O$_2$ at 600K for 60 min. The sample bias is 1 V, the tunnelling current is 0.1 nA.
Chapter

4 Oxidation of Pd(110) in Dioxygen : From Low to High Pressure
Abstract

Oxidation of Pd(110) in low pressure (< 10^{-6} Torr) and high pressure (1-150 Torr) O_{2} was characterized by Scanning Tunneling Microscopy (STM), Auger-electron Spectroscopy (AES), Temperature Programmed Desorption (TPD) and Low Energy Electron Diffraction (LEED). A Pd(110)-c(2×4)-O reconstructed superstructure was induced upon initial oxygen chemisorption. The formation of an intermediate surface oxide characterized by a complex LEED pattern was observed following 12 L NO_{2} or 2,500 L O_{2} dosing at 550 K. Maximum oxygen coverage of 1.8 ML was attainable by exposing to either 100 L NO_{2} or 8,000 L O_{2} at 550 K. Oxidation of Pd(110) in high pressure O_{2} resulted in the dissolution of surface chemisorbed oxygen into Pd near surface region and subsequently the formation of bulk PdO. The oxidation rate was limited by the diffusion of oxygen through PdO, which followed the Mott-Cabrera parabolic diffusion law. STM imaged the Pd(110) surface morphology transformation during the oxidation. Exposure to 1 Torr O_{2} led to the growth of island structure. The inter-planar spacing for the first two surface layers was expanded by 0.1-0.3 Å. Elongated oxide agglomerates along <1Ì0> nucleated and grew on Pd(110) surface after oxidation in 5-25 Torr O_{2} at 600 K. A bulk PdO was formed characterized by the complete fading out of Pd(110) (1×1) LEED pattern, the O/Pd atomic ratio of 0.3-0.7 and the amorphous “cauliflower-like” surface structure composed of semi-spherical agglomerates 3.0-5.0 nm in size. The surface roughening was accelerated by increasing the oxygen pressure and/or the oxidation temperature.
4.1 Introduction

Palladium has been considered to be an excellent catalyst for oxidation reactions in both metallic and oxide forms. Application of the catalyst involves complete oxidation of hydrocarbons in automotive catalytic converters and catalytic methane combustion in advanced gas turbines with low thermo-generated NO\textsubscript{x} emissions [1]. Compared with other transition metal catalysts for example Pt/Rh, Pd is more economical and has the highest turnover rate (rate per active site) [2].

Despite the industrial importance of Pd-based catalysts, their complex behaviors in realistic reaction environments have not been well understood. One of the challenges is related to the interaction of Pd metal with oxygen especially in the pressure/temperature range for realistic CH\textsubscript{4} combustion [3-5]. The interaction of oxygen with palladium single crystals in high-vacuum conditions (<10\textsuperscript{-6} Torr) has been studied extensively in previous research, see for instance [6-15] and references therein. Therefore, this project is proposed to characterize the oxidation mechanism of palladium under the oxygen pressure/reaction temperature close to CH\textsubscript{4} combustion conditions using Scanning Tunneling Microscopy (STM), along with Temperature Programmed Decomposition (TPD), Auger-electron Spectroscopy (AES) and Low Energy Electron Diffraction (LEED). The results on oxidation of Pd(110) single crystal are presented in this paper.

Prior work has shown that exposure of Pd(110) to oxygen in high vacuum conditions resulted in a variety of superstructures ranging from (2\times3)1D, (1\times2), (1\times3), c(2\times4), c(2\times6) to more complex structure [9, 11, 16-18] depending on the adsorption temperature and the amount of exposure. Among the six oxygen-induced reconstructions, the c(2\times4)
phase, stable at a temperature between 400-700 K, could be formed by either a few Langmuirs (0.8-3 L, 1 L = 10^{-6} Torr s, 1 Torr = 133.3 Pa) of oxygen exposure at temperatures of 400-600 K [9, 13, 16, 19], or by cooling the sample in an oxygen pressure of 10^{-9}-10^{-8} Torr to 470-500 K in a time frame of several minutes, following initial flashing at 720-1100 K [20, 21]. The oxygen coverage on Pd(110)-c(2×4)-O was determined to be 0.50 ± 0.05 monolayer (ML, 1 ML = 9.35 × 10^{14} atoms cm^{-2}) or > 1 ML, where the 0.5 ML coverage stood for the saturation of the surface adsorbed oxygen [22] and the further oxygen uptake was suggested to populate the subsurface region [10]. At even higher oxygen exposure, for example exposing the single crystal sample to 60 L oxygen at temperature between 900 K and 500 K (during cooling), a non-crystalline and “sponge-like” surface structure was revealed in a STM experiment by Niehus and Achete [21]. Palladium oxide started to form after the oxidation of Pd(110) in 3 × 10^{-2} Torr O_2 for 20 min at a sample temperature of 400 K [23]. Kinetic studies using X-ray Photoelectron Spectroscopy (XPS) and TPD for the initial oxidation suggested a temperature-deactivated process in the temperature range from 340 K to 420 K, where the initial oxidation rate was higher at lower temperature than that at higher temperature [23].

Differing from the previous work, the experimental approach in the present investigation is to study the kinetics for the oxidation of Pd(110) in high oxygen pressures ranging from 1-150 Torr and sample temperatures between 600-780 K. The various surface structures at different oxidation steps up to the regime where bulk PdO forms are characterized and compared to the surface chemisorbed oxygen overlayers. It will be shown that the oxidation of Pd(110) proceeds through a three-step mechanism including chemisorption of oxygen, diffusion of oxygen into Pd metal, and the formation of bulk
PdO. The oxygen uptake on Pd(110) during oxidation increases with the O$_2$ pressure, the treatment temperature and the exposure time. PdO only resulted when a critical concentration of oxygen atoms is reached in the near surface region. The surface morphology of Pd(110) also changes as a function of oxidation conditions. Increase the O$_2$ pressure, the Pd(110) surface experiences three major expansions including the fading out of the atomic features, the growth of elongated agglomerates along $<1\overline{1}0>$ direction and the formation of “cauliflower-like” structure by aggregating semi-spherical agglomerates. The insight into the Pd oxidation mechanism in the conditions of high O$_2$ pressure and high temperature in this work is expected to allow for a better catalytic performance of Pd-based catalysts in practical applications.

4.2 Experimental Methods

The experiments were carried out in a specially designed system consisting of three stainless steel chambers: an Ultra-High Vacuum (UHV) analysis chamber, a UHV STM chamber and a high-pressure reaction cell. The analysis chamber housed facilities for AES, LEED, and TPD. The STM chamber accommodated an ambient-temperature UHV STM (RHK Inc.). The base pressure in UHV chambers after baking out was $5 \times 10^{-10}$ Torr ($1$ Torr = 133.3 Pa). The high-pressure reaction cell served for high-temperature/high pressure treatments had a base pressure of $2 \times 10^{-8}$ Torr.

The sample was a 1 mm thick, 8.5 mm diameter single crystal Pd(110) (Princeton Scientific Corp.) with misalignment $< 0.5^\circ$. The single crystal was mounted on a standard RHK sample holder. Sample temperature was measured by a chromel-alumel thermocouple spot-welded onto the side of the single crystal. In the analysis chamber,
the sample was heated by electron-bombardment from the rear. In the reaction cell, the sample was heated by an IR lamp.

The TPD spectra were collected by means of a RGA-200 mass-spectrometer (Stanford Research System, Inc.) at a constant heating rate of 5 K s\(^{-1}\). The coverage was calculated by integrating the area under the TPD peak and calibrated to monolayers by the ideal 0.5 ML coverage on a surface that was saturated with chemisorbed oxygen by 12 L O\(_2\) dosing at 550 K and presented a c(2×4) LEED structure [9, 22].

The sample cleaning procedure consisted of repeating cycles of Ar\(^+\) sputtering at room and elevated temperatures, flashing up to 1000 K, exposure to O\(_2\) and NO\(_2\) followed by annealing at 1000 K for 60 seconds under UHV conditions. The sample cleanliness was checked by TPD, AES and LEED. NO\(_2\) and O\(_2\) were introduced into the analysis chamber through a capillary doser.

The STM images were obtained using Pt-Ir tips electrochemically etched in NaCl/NaNO\(_3\) (molar ratio 1:4) melt at around 400-450 °C. Sample biases with respect to the tip of 0.1-1 V and tunneling currents of 0.1-1 nA were applied for all images shown. Surface area increase after oxidation of the Pd(110) single crystal was determined from analysis of the STM images by taking the discrete image pixels and joining them by a series of triangles. Integration of the area of individual triangle gives the total area [24].

The following experimental protocol was used for oxidation experiments. The single crystal was heated to the desired temperature in vacuum and then oxygen was introduced. After oxidation, the sample was cooled and oxygen was pumped out simultaneously. It took less than 1 min to reduce the sample temperature to 450 K and to reach the vacuum in the reactor better than 10\(^{-6}\) Torr. After a treatment, the sample could be transferred
into the STM and/or analysis chamber by means of a 142 cm transfer arm without contact with atmosphere.

4.3 Results

4.3.1 Clean Pd(110) surface

Clean Pd(110) has well-defined rectangular LEED pattern as shown in Figure 4.1(a). The measured nearest atom spacing along $<1\overline{1}0>$ was $2.7 \pm 0.1$ Å (theoretical spacing is 2.75 Å), and along $<001>$ $3.9 \pm 0.1$ Å (theoretical value is 3.89 Å). The STM image (Figure 4.1(b)) obtained on this smooth surface demonstrates a $(1\times1)$ surface structure on the terraces, where the distance between two nearest neighbor rows along $<001>$ is about 3.9 Å.

4.3.2 Pd(110)-c(2×4)-O superstructure

Exposure of the single crystal Pd(110) to 12 L O$_2$ at 550 K resulted in the Pd(110)-c(2×4)-O surface reconstruction, which is characterized by the sharp $1/2$-fractional-order spots between the integral-order spots along the $<001>$ and $1/4$-order and $3/4$-order spots along $<001>$ in the half-order positions along $<1\overline{1}0>$ as shown in Figure 4.2(a) and (b). STM images of the c(2×4) phase was obtained in an oxygen base pressure of $5 \times 10^{-9}$ Torr. Since it normally took about 60 min to transfer the sample to the STM chamber, allow the sample to cool to room temperature (RT) and bring the tip into tunneling range, in order to preserve the surface c(2×4) oxygen structure or it might be reduced by residue H$_2$ and CO to Pd(110) $(1\times2)$, the O$_2$ base pressure was maintained in the chambers before and during the scanning.
A large-scale survey of the reconstructed surface was shown in Figure 4.3(a). Clearly, the surface was composed of a large number of rows parallel along $<1\bar{1}0>$. The spacing between adjacent bright or dark rows was found to be $8.1 \pm 0.5 \text{ Å}$ or twice the lattice distance in the $<001>$ direction. Totally four layers of mesoscopic terraces were distinguishable separated by monoatomic steps. Several domain boundaries and missing Pd atom defects were visible and marked out as point “a”.

High resolution STM image obtained on this superstructure was consistent with the LEED observation as shown in Figure 4.3(b), in which the group of atoms marked by the rectangle displays a unit structure. The two adjacent protrusions along $<1\bar{1}0>$ was mostly close to $5.5 \pm 0.5 \text{ Å}$ apart, which was approximately twice the distance $d_{<1\bar{1}0>}$ and the distance measured between two nearest neighbor rows along $<001>$ was around $7.9 \pm 0.1 \text{ Å}$, roughly twice the distance $d_{<001>}$. It was also noted that adjacent $<001>$ rows were shifted by one lattice spacing $d_{<011>}$ indicating the c(2×4) pattern. The STM image described here was observed previously by Niehus and Achete [21]; whereas, different STM experiments by Bennett et al. [20] and Tanaka et al. [13] suggested only one time periodicity along the $<1\bar{1}0>$ direction.

The corrugation measured along the $<001>$ direction on the Pd(110)-c(2×4)-O surface confirmed the proposed Pd(1×2) missing/added row reconstruction structure [13, 20, 21]. We measured a corrugation of 0.8-0.9 Å in the missing/added row. This was similar to the c(2×6), c(2×8), c(2×10) and (2×2)p2mg structures on Rh(110)-O, where the STM determined the corrugation of 0.7-0.82 Å in the missing row [25]. Further evidence was found on the (1×2) missing-row structure of oxygen induced Au(110) reconstruction, which had a corrugation of 0.8 Å [26] and on the c(2×4) added-string structure of
Ni(110)-O with the corrugation of 0.8 Å [27]. However, the corrugation in the protruding row along <1\bar{1}0> direction was determined to be 0.4-0.5 Å, almost doubled that measured on the reconstructed Rh(110)-O surface of only 0.16-0.2 Å [25] and on the Ni(110)-O surface of less than 0.2 Å [27]. The interpretation of this Pd(110)-c(2\times4)-O superstructure will be a subject of another publication [28].

TPD spectrum of the c(2\times4) superstructure shows a peak maximum at 810 K in Figure 4.4(a) which corresponds to the desorption of surface chemisorbed oxygen as suggested by He and Norton [10].

4.3.3 NO\textsubscript{2} adsorption

On palladium surfaces, NO\textsubscript{2} dissociatively adsorbs below room temperature yielding NO and O. At above 500 K, the NO desorbs leaving atomic oxygen on the surface [7, 14, 15]. Figure 4.4(b) shows the O\textsubscript{2} TPD trace following an exposure of Pd(110) to 12 L NO\textsubscript{2} at 550 K. The oxygen coverage on this surface was about 1.2 ML. The two shoulder peaks located at 685 K and 725 K were assigned to the decomposition of a surface palladium oxide [8]. The intensities of the two peaks decreased after residing the sample in the UHV chambers due to the reduction by the residual CO and H\textsubscript{2} gases.

A complicated LEED pattern was revealed after the 12 L NO\textsubscript{2} exposure as shown in Figure 4.5(a). The schematic diagram in Figure 4.5(b) demonstrates the positions of the integral and the fractional spots. This complex LEED pattern diffused when the temperature was raised above 500 K during TPD and was completely replaced by Pd(110)-c(2\times6)-O surface reconstruction at around 550 K. By heating the sample up to 600-700 K Pd(110)-c(2\times6)-O transformed into sharp Pd(110)-c(2\times4)-O. As the sample
was heated to above 700 K, Pd(110)-(2×3)-1D LEED pattern was observed. Pd(110) (1×1) resulted only at a temperature above 750 K. This surface structure transformation procedure as a function of oxygen desorption temperature was almost identical to that previously described by Nishijima et al. [11] after exposing Pd(110) to 3 L oxygen followed by heating the sample from 100 K to 900 K.

Unfortunately, the high reactivity of the surface oxygen with residual gases precluded imaging the surface structure with STM, only the c(2×4) overlayer was observed, see Figure 4.6(a). We tried to preserve the surface oxygen phase by maintaining an oxygen background pressure of $5 \times 10^{-9}$ Torr in the chambers, but the effort was not successful.

It has been reported that for Pd(111), exposure to NO$_2$ allowed access to oxygen coverages an order of magnitude higher than could be obtained by O$_2$ exposure [14]. While, on Pd(100), the maximum oxygen coverage of 0.8 ML was attainable by exposure to either NO$_2$ or O$_2$, except that the NO$_2$ dosing required to reach this coverage was almost two order of magnitude lower [15]. It was found out in this work that raise the O$_2$ or NO$_2$ dosing could both lead to an increase in the oxygen coverage. Unlike the Pd(111), but similar to Pd(100), the maximum oxygen coverage of 1.8 ML was obtained following exposure to 100 L NO$_2$ or 8,000 L O$_2$ at 550 K. In addition, the complex LEED pattern mentioned above could also be observed after dosing 2,500 L O$_2$ at 550 K. Therefore, the Pd(110) surface should also have a higher reactivity towards O$_2$ than the Pd(111) surface.

After exposure to 250 L NO$_2$, a relatively rough surface appeared with a 2% surface area increase. The structure looked as if it was covered with islands that were composed of rows of small agglomerates about 1 nm in size along $<1\overline{1}0>$ direction, although the agglomerate shape was not quite obvious since the edges were blurred (Figure 4.6(b)).
Islands were separated by steps with the depth being mostly 1.2-1.4 Å, but could also be measured to be about 2.6-3.0 Å. Thus, basically still mono- and a few double-atomic steps occurred on this surface.

4.3.4 Oxygen uptake after high-pressure (1-150 Torr) O\textsubscript{2} treatment

4.3.4.1 O\textsubscript{2} pressure effect

Pd(110) was oxidized at elevated sample temperatures of 600, 650 and 700 K in the O\textsubscript{2} pressure range 1-150 Torr for a constant time interval of 10 min. The oxygen uptakes after different treatments were measured in monolayers and plotted as a function of O\textsubscript{2} pressure in Figure 4.7. It was found that at 600 K the uptake increased with O\textsubscript{2} gas phase pressure up to 50 Torr. The relation could be summarized as:

\[
N_{\text{oxygen}} \propto P_{O_2}^{0.2}
\]  

(1)

Above 50 Torr, the uptake rate fell off and appeared to be almost independent to the O\textsubscript{2} pressure. Increasing the O\textsubscript{2} treatment temperature would lower the pressure at which the transition occurred. The oxygen uptake became zero order in pressure at 650 K in O\textsubscript{2} above 5 Torr and at 700 K in O\textsubscript{2} above 1 Torr. It should be noted that the oxygen uptake pressure independence was accompanied with the complete fading out of the Pd(110) (1×1) LEED pattern and the appearance of roughening surface structure composed of semi-spherical agglomerates as will be discussed in detail later on.
4.3.4.2 Oxidation time effect

The oxygen uptake on Pd(110) increased as the time for oxygen exposure extended. Figure 4.8 through 4.10 represent the oxygen uptakes after oxidation of Pd(110) for various time interval between 1-160 min. Clearly, a two-step mechanism was distinguished (Figure 4.9), in which the moment for the transition to occur depends on the O$_2$ pressure and treatment temperature. For the sake of expression, the two steps are designated as step-I and step-II in the following context.

In step-I, for a short period of time, the oxygen uptake was linearly proportional to the square root of the time of reaction as shown in Figure 4.8. The time dependence of the oxygen uptake thus could be described by the diffusion controlled Mott-Cabrera parabolic law [29]:

\[
N_{\text{oxygen}} = K_1(T, P) \cdot t^2
\]

Here $K_1$ is the parabolic rate constant and as has been illustrated in the Figure 4.8 a function of O$_2$ pressure (only at 600 K) and sample temperature. Despite the large amount of oxygen uptake on the sample, for example 60 ML after oxidation at 650 K for 30 min and 40 ML at 780 K for 1 min in this step, the Pd(110) (1×1) LEED pattern with slightly diffused diffraction spots was observed; and no essential amount of oxygen (< 5%) was detected with AES.

Differing from the step-I, in the step-II oxidation of Pd(110) for a long period of time experienced a considerably dropping in the O$_2$ uptake rate as shown in Figure 4.9(a) and
(b). The time dependence of oxygen uptake could be well expressed as (see Figure 4.10(a) and (b)):

\[
N_{\text{oxygen}}^2 - N_{\text{oxygen}_0}^2 = K_2(T)^2 \cdot (t - t_0)
\]  

(3)

Here \(K_2\) is the rate constant in this step, \(t_0\) is the starting point for the transition from step-I to step-II and \(N_{\text{oxygen}_0}\) is the oxygen uptake at \(t_0\). Apparently, \(K_2\) was not a strong function of \(O_2\) pressure even at 600 K, since similar \(K_2\) was obtained after oxidation of Pd(110) at 600 K in 10 Torr and in 50 Torr \(O_2\) (Figure 4.10(a)). But it increased with the sample temperature as shown in Figure 4.10(b). The rate expression in equation (3) suggested that the oxygen uptake in this step also obeyed the Mott-Cabrera parabolic diffusion law, except that the parabolic rate constant \(K_2\) was smaller than \(K_1\) in step-I.

After the \(O_2\) treatment in step-II, no Pd(110) (1×1) LEED pattern was observable and AES determined the O/Pd atomic ratio around 0.3-0.7. Intensive roughening of the sample surface was revealed by STM (see for example, Figure 4.13 and Figure 4.15).

### 4.3.4.3 Sputtering effect

Surprisingly, a pronounced sputtering effect was observed. The amount of oxygen uptake on a freshly-cleaned (Ar\(^+\) sputtering followed by annealing to 1000 K) Pd(110) single crystal was noticeably lower than the stable value, which was obtained by repeating the \(O_2\) exposure until no substantial increase was detected. The comparison was provided in Table 4.1. The reason for this phenomenon was not clear yet, but it could be related to the depletion of oxygen in the palladium bulk region by Ar\(^+\) sputtering [30].
4.3.5 Surface morphology after high-pressure (1-150 Torr) O₂ treatment

4.3.5.1 O₂ pressure effect

Structural changes on the Pd(110) surface after oxidizing the single crystal was studied by Scanning Tunneling Microscopy. Figure 4.11(a) through (g) show the sets of typical STM images obtained after treatments in 1, 5, 10, 25, 50, 100 and 150 Torr O₂ at 600 K for 10 min. Clearly, increasing the O₂ pressure led to the roughening of the surface morphology and the surface structure experienced three major expansions as the pressure was raised stepwisely.

A survey on the Pd(110) surface after an exposure to 1 Torr O₂ at 600 K for 10 min is shown in the STM image of Figure 4.11(a)-1, which is evidently different from a clean Pd(110) surface, but shares some similarities with the surface after an exposure to 250 L NO₂ at 550 K (Figure 4.6). A mesoscopic ordered island structure (“checkerboard-type” pattern) composed of alternating bright and dark islands appeared after this O₂ treatment. The mean size of the bright island was estimated to be about 7 and 15 nm in the <001> and <110> directions respectively. It was noted that the height difference between individual bright and dark islands was measured to be 1.4-1.7 Å, slightly higher than the monoatomic step on Pd(110). A close up STM image on this surface in Figure 4.11(a)-2 shows that the distance between two nearest neighbor rows on a particular island is still around 8 Å, similar to that on a Pd(110)-c(2×4)-O surface.

Raising the O₂ pressure to 5 Torr induces the nucleation and growth of rod-shaped agglomerates with aspect ratio 2.5:1-4.0:1 as shown in Figure 4.11(b). These agglomerates were prone to grow parallel to one another with the elongated side along
the $<1 \overline{1} 0>$ direction. The size of the agglomerates was $3.0 \pm 0.5$ nm in length and $1.6 \pm 0.3$ nm in width, which as can be seen in Figure 4.11(c) and Figure 4.11(d) only slightly changed with the $O_2$ pressure up to 25 Torr. The agglomerate sizes on the surface after exposure to 10 Torr and 25 Torr $O_2$ were $3.3 \pm 0.6$ nm vs. $1.9 \pm 0.4$ nm and $3.7 \pm 0.6$ nm vs. $1.7 \pm 0.5$ nm respectively. Zooming into the individual agglomerates revealed no evidence of atomic scale features.

Bulk PdO formation starts following the oxidation of Pd(110) in 50-150 Torr $O_2$ as shown in Figure 4.11(e) through (g). The surface underwent a major reconstruction, which resulted in the complete loss of the mesoscopic ordering of the surface structure and the growth of semi-spherical agglomerates. These oxide agglomerates tended to aggregate to form a “cauliflower-like” superstructure, although not quite clear in the images shown. The size of the agglomerates increased slightly with the $O_2$ pressure, being $3.2 \pm 0.4$ nm and $4.5 \pm 0.6$ nm at 50 and 150 Torr respectively. Judging from the STM images, the structure still showed a slightly preferential growth orientation along the $<1 \overline{1} 0>$ direction.

The increase in the Pd(110) surface area after 1-150 Torr $O_2$ treatments is estimated by SM image analysis and illustrated in Figure 4.12. As expected from the surface morphologies shown in Figure 4.11(a) through (g), the surface area did not increase linearly with the $O_2$ pressure, but rather fell into three distinct regions at low ($P_{O_2}$ around 1 Torr), intermediate ($P_{O_2}$ in the range of 5-25 Torr) and high pressures ($P_{O_2} > 50$ Torr). Surface area increased about 2-5% after oxidation in the low-pressure regime. A 10-20% expansion of the surface was measured after a treatment in the intermediate-pressure region. And a 25-40% area increase was determined for the high-pressure regime. The
increase in palladium surface area by oxidation has been reported for Pd foil [31] and supported Pd samples [32] in literatures.

### 4.3.5.2 Oxidation time effect

It was found that extension of the oxidation time also lead to the roughening of the surface as shown in Figure 4.13(a)-(c) in 10 Torr O₂ at 600 K. The reconstruction of Pd(110) surface involves three steps as well, including the blurred atomic scale features (< 10 min), growth of elongated agglomerates paralleling along \(< 1\bar{1}0 >\) direction (10-30 min), and the formation of semi-spherical agglomerates 3.5 ± 0.6 nm in size (60 min). After the 60 min O₂ treatment, the entire surface was imaged to possess a similar structure obtained after oxidation in 50-150 Torr O₂ at 600 K for only 10 min as shown in Figure 4.11(e)-(g), except that this surface presented a more clear “cauliflower-like” superstructure. The surface area increase shown in Figure 4.14 was also in consistent with the STM observations.

### 4.3.5.3 Oxidation temperature effect

Raising the Pd(110) oxidation temperature could accelerate the surface roughening process. STM images in Figure 4.15 illustrate the surface structures after oxidation of the single crystal at 700 K in 1 and 10 Torr O₂ for 10 min. Figure 4.15(a), similar to Figure 4.11(b)-(d) (obtained by oxidation in 5-25 Torr O₂ at 600 K for 10 min), shows slightly elongated agglomerates growing along \(< 1\bar{1}0 >\) direction after a treatment in 1 Torr O₂ at 700 K. The agglomerate size was about 3.7 ± 0.6 nm in length and 2.3 ± 0.5 nm in width with an aspect ratio close to 1.5:1. Figure 4.15(b), similar to Figure 4.13(c) (obtained by
oxidation in 10 Torr O$_2$ at 600 K for 60 min), shows a surface covered by semi-spherical agglomerates 5.5 ± 0.5 nm in size after an exposure to 10 Torr O$_2$ at 700 K. In this higher temperature treatment case, a clear “cauliflower-like” superstructure 10-15 nm in size appeared by aggregating small agglomerates. The area increase after the treatments at 700 K in 1 Torr and 10 Torr O$_2$ was estimated to be 18% and 44%, respectively.

4.3.6 Alternating oxidation procedure

Exposure of Pd(110) to 1 Torr O$_2$ at temperatures between 600 and 780 K for short period of time for example 1-5 min followed by quenching in vacuum resulted in only slightly diffused Pd(110) (1×1) LEED patterns. It was found that a complex LEED pattern identical to that obtained after 12 L NO$_2$ adsorption at 550 K would be observed when the sample was quenched in O$_2$ after the high-pressure exposure. In addition AES also detected the oxygen signal, and the O/Pd atomic ratio was around 0.07. This complex LEED pattern decayed in UHV in less than 1 hr due to the reduction by background H$_2$ and CO.

4.4 Discussion

4.4.1 Palladium oxidation mechanism

The combined STM, LEED, AES and TPD results suggest that the oxidation of Pd(110) proceeds through a three-step mechanism including the chemisorption of oxygen atoms, diffusion of adsorbed oxygen into the palladium metal and the stoichiometric PdO formation. The deduction of the mechanism could be understood as follows. The heat involved upon dissociative adsorption of oxygen on Pd(110) surface was suggested to be
in the range of \(-334 - \text{–}200 \text{ kJ mol}^{-1}\), with the highest value on the lowest oxygen coverage surface (about 0.18-0.2 ML) [33], which is considerably higher than \(-107 \text{ kJ mol}^{-1}\), the heat of formation of PdO at 1050 K [5]. Therefore, initial exposure of Pd(110) to O\(_2\) would only result in the chemisorption of oxygen atoms. Like the (110) surface of most face centered cubic (fcc) transition metals, for example Rh(110) [34], Pd(110) also shows a strong tendency to reconstruct in the presence of oxygen adsorbate. A Pd(110)-(2×4)-O reconstructed structure is induced upon oxygen adsorption, with a saturated surface coverage of 0.5 ML. The oxygen uptake could be further increased to above 1 ML by exposure to a stronger oxidant such as NO\(_2\) or by using higher O\(_2\) pressure. Accommodation of the O atoms requires compression of the adsorbate layer, which lowers the oxygen binding energy and thus makes the penetration of adsorbed oxygen into Pd metal energetically favorable [30]. There is no evidence for the formation of bulk PdO after the initial atomic oxygen bulk diffusion. Only Pd(110) (1×1) LEED pattern referred as the bare metallic surface was revealed and AES detected O/Pd ratio less than 5% after exposure of Pd(110) in 1 Torr O\(_2\) at 600 K for 10 min; in addition, a surface structure close to Pd(110)-(2×4)-O reconstruction was imaged using STM (Figure 4.11(a)). A metastable, two-dimensional surface oxide that is suggested to be intermediate between Pd and PdO could be formed, which exhibits characteristic structures distinct from either Pd metal or Pd oxide on Pd(111) and Pd(110). On Pd(111) surface, STM images on this 2D surface oxide along with a complex LEED pattern was reported by Zheng and Altman [14] following an exposure to 8.1 L NO\(_2\) at 575 K. A similar LEED structure was reported on Pd(111) by Voogt et al. [35] after an O\(_2\) exposure > 15,000 L at 620 K followed by cooling to RT in 10\(^{-5}\) Torr O\(_2\). On Pd(110)
surface, a complex LEED pattern corresponding to the surface oxide was observed after 12 L NO₂ dosing or 2,500 L O₂ dosing at 550 K. It has been suggested that this oxide metastable phase could be “frozen in” by reducing the sample temperature in O₂ pressure [35]. Thus, the complex LEED patterns for the surface oxide on Pd(111) and Pd(110) also appeared after exposure the single crystal surfaces to high-pressure oxygen (1-10 Torr) followed by quenching in the O₂ pressure [36]. The reason for the formation of this metastable oxide phase is not quite clear yet. But it must relate to the three interactions -- between the O atoms and Pd atoms on the surface; between the O atoms on the surface with the underlying Pd atoms that are either bound or not to oxygen atoms; between the O atoms in the near surface region and the Pd atoms on the surface.

The penetration of oxygen atoms requires expansion of the metallic Pd lattice structure to accommodate interstitial oxygen atoms. Therefore, when Pd(111) was treated in 1-25 Torr O₂ at 600 K, the monatomic step height increased by 0.2-0.4 Å from the original 2.25 Å [36]; whereas on Pd(110), the inter-planar spacing for the first two surface layers was raised by 0.1-0.3 Å from the ideal monoatomic height of 1.38 Å after an exposure to 1 Torr O₂ at 600 K. The diffusion of adsorbed oxygen was also evidenced by a negative work function change [10].

Clearly, bulk Pd oxide would finally result starting from the surface when the oxygen concentration reached a “critical” value in the near surface region. The formation of PdO likely goes through a nucleation mechanism [14]. Small oxide agglomerates appeared on the Pd(111) surface after oxidation in 25 Torr O₂ at 600 K for 10 min [36]; whereas, on Pd(110), a number of elongated oxide agglomerates were observed aligning along <110> direction following the oxidation in 5-25 Torr O₂ at 600 K (Figure 4.11(b)-(d)).
Possible reason for the elongated oxide agglomerate shape is as follows. Oxygen adsorption on Pd(110) induces the missing/added row surface reconstruction along <001> [13, 20, 21]. The adsorbed oxygen atom is suggested to reside in only one kind of binding site that is either the hcp (above the second layer) [13, 16-18, 20] or the fcc (above the third layer) [21] three-fold hollow site on the added Pd row along <110> direction. Thus, the higher density of oxygen atoms as compared to along <001> initiates the oxide nucleation and growth along <110>. The oxide overlayers formed after oxidation in 5-25 Torr O₂ at 600 K was thin as only slightly diffused metallic Pd(110) (1×1) LEED pattern was observed, which reflected the metallic Pd(110) structure underneath. The 5 Å inelastic mean free path for electron in Pd metal at 73 eV, which is the beam voltage used for all LEED patterns in this work, suggested that the average thickness of the oxide layer was about 2 ML. Whether this thin oxide layer would passivate the bulk diffusion of oxygen atoms or not is not clear yet, but the oxygen diffusion rate in the thin oxide layer obeyed the Mott-Cabrera parabolic law and was higher than that in the bulk PdO (Figure 4.8-4.10).

The formation of bulk PdO was characterized by the drastically dropped oxygen uptake rate, the complete fading out of the metallic Pd(110) LEED pattern, the 0.3-0.7 O/Pd atomic ratio detected by AES and the roughened amorphous surface structure imaged using STM with a surface area increase by a factor of >20%. The formation of the bulk oxide strongly depends on the oxidation conditions. The bulk PdO formed in a shorter time in a higher O₂ pressure or at a higher temperature. That was why a rough surface was imaged with an area increase above 30% following oxidation for 10 min in 150 Torr O₂ at 600 K (Figure 4.11(g)) or in 10 Torr O₂ at 700 K (Figure 4.15(b)) but for 60 min in
10 Torr O₂ at 600 K (Figure 4.13(c)). Once the bulk PdO was formed, the oxygen uptake rate also referred as the oxidation rate was limited by the diffusion of oxygen through the bulk oxide phase. It is well known that oxide is a diffusion barrier for oxygen, thus a considerably dropped oxidation rate was expected at the moment of PdO formation (Figure 4.9). This rationalizes the two steps distinguished in the oxygen-uptake time effect. The oxygen sticking coefficient is suggested to be significantly higher on the oxide surface compared with metallic surface [37]. Thus, it is reasonable to assume that the oxide surface is saturated with oxygen and then the diffusion in the oxide should be O₂ gas phase pressure independent. This explains the observed oxygen-uptake pressure effect that the oxygen uptake does not increase with the O₂ pressure after an exposure to above 50 Torr of O₂ at 600 K and above 5 Torr at 650 K (Figure 4.7).

4.4.2 Comparison between oxidation of Pd(111) and Pd(110)

Oxidation of Pd (110) shows many similarities to Pd(111) oxidation. Initial exposure of both surfaces at RT or elevated temperatures to O₂ in the pressure range of 10⁻⁸ Torr leads to the dissociative oxygen adsorption [6, 14]. As the oxygen uptake increases by NO₂ or high pressure O₂ exposure, a metastable surface oxide is formed characterized by a complex LEED pattern [11, 15, 33, 35]. Oxidation of both surfaces in O₂ pressure 1-150 Torr at temperature 600-800 K, the oxygen uptake is found to increase as the pressure rises from 1-50 Torr at 600 K. The oxygen uptake rate follows the Mott-Cabrera parabolic law. During the oxidation, both surface structures experience three major expansions as the pressure increases stepwisely from 0-1 Torr, 5-25 Torr and 50-150 Torr. Surface area is increased consistent with the surface roughening. Only amorphous structure composed of semi-spherical agglomerates is imaged on a completely oxidized
surface [36]. There are, however, also some differences between the oxidation of the two surfaces. First, the (110) surface is more reactive towards $O_2$ than Pd(111). The maximum oxygen coverage was attainable by exposing to both NO$_2$ and O$_2$ in high vacuum conditions. Further, Pd(110) tends to reconstruct upon oxygen adsorption, which results in a variety of superstructures. Oxidation in high pressure O$_2$ (1-150 Torr), the more open surface structure of Pd(110) allows a higher atomic oxygen diffusion rate than can be obtained on Pd(111). At 600 K, an equivalent of 20 ML of oxygen uptake was measured on Pd(110) after an exposure to 10 Torr O$_2$ for 10 min, compared with the 11 ML uptake on Pd(111). This result is approximately inversely proportional to the surface atomic densities which on Pd(110) is $9.4 \times 10^{14}$ atoms/cm$^2$, and on Pd(111) $1.53 \times 10^{15}$ atoms/cm$^2$. A direct consequence of the fast diffusion is that the formation of PdO proceeds at higher oxygen uptake on Pd(110). Also, the densely packed Pd(111) surface needs more expansion than Pd(110) during oxidation to accommodate the 60% decrease in the Pd volumetric density in PdO. This explains a 87% surface area increase on Pd(111) compared to the 30% on Pd(110) after oxidation in 100 Torr $O_2$ at 600 K for 10 min.

### 4.4.3 Structural sensitivity for CH$_4$ combustion over Pd catalyst

Returning to catalysis, the structure sensitivity for CH$_4$ combustion over Pd catalyst typically in the condition when PdO is the active phase is an issue not yet resolved [32, 38-43]. To address this question, we need to characterize the surface structures on Pd catalyst after subject to CH$_4$ combustion. In this analogous work, the surface morphologies on Pd single crystal (111) [36] and (110) were imaged using STM after oxidation in high pressure (50-150 Torr) $O_2$ at 600 K, a condition comparable to a
realistic CH$_4$ combustion. Both surfaces revealed a “cauliflower-like” structure composed of semi-spherical agglomerates after the treatment irrespective of the original facets. The fact that no discernible crystalline order was outlined by STM, combining with the LEED observations that did not show any patterns, gives the indication that only amorphous PdO is formed. Thus, the CH$_4$ combustion might be insensitive to the oxide structure.

4.4.4 Activation of Pd catalyst for CH$_4$ combustion

CH$_4$ combustion over Pd supported catalysts requires an activation period before a steady state reaction rate is reached. In the literature, this behavior has been suggested due to the presence of impurities [44, 45], the interaction with supports [38] the transformation between different sample oxidation states [41, 46], or the morphology change of Pd crystallites [47]. It was found out in a recent work by our group that CH$_4$ combustion over Pd(111) and Pd(110) single crystals also presented a lower rate in the initial combustion stage [36]. The reaction rate on a Pd(111) surface for CH$_4$ combustion in lean condition (600 K, 16 Torr CH$_4$, 160 Torr O$_2$ and N$_2$ balance to 800 Torr, the experimental procedure was identical to that on a Pd polycrystalline foil, see reference [31]) measured 5 min after the beginning of the reaction was only 1/5 of the steady state rate. Similar to a Pd(110) surface, the initial rate was 1/4 of the steady state rate [36]. Since there was no support present, the reactivity was definitely not affected by the metal-support interaction. Moreover, X-ray Photoelectron Spectroscopy (XPS) did not detect any noticeable amount of impurities on the single crystal surfaces before and after the reaction [36]. Thus, the only possibility left is the slow PdO formation rate. It was noted that at 600 K under an oxygen pressure of 10 Torr, bulk oxide was not formed in
the first 1-30 min and the surface retained a semi-ordered structure (Figure 4.11). This lagged period in Pd oxidation could correspond to the activation period in CH$_4$ combustion due to the relatively smaller surface expansion or the existence of metallic Pd on the surface.

A previous study from our group however suggested almost no activation period for CH$_4$ combustion over a Pd polycrystalline foil [31]. This was understood by the higher PdO formation rate on foils than on the single crystals. The oxide formation process was accelerated because of the dense defects on Pd foils, which acted as oxygen adsorption sites and the oxide nucleation sites.

4.5 Summary

Oxygen oxidation of a Pd(110) single crystal surface was studied in two pressure regimes: low pressure (<$10^{-6}$ Torr) and high pressure (1-150 Torr). Clean Pd(110) surface has a well defined rectangular unit structure. A Pd(110)-c(2×4)-O reconstruction was induced upon adsorption of 0.5 ML O$_2$ at 570 K. Exposure to 12 L NO$_2$ or 2,500 L O$_2$ at 550 K resulted in the formation of an intermediate surface oxide which was characterized by a complex LEED pattern distinct from PdO or Pd(110). The maximum 1.8 ML oxygen uptake was attainable by increasing the NO$_2$ exposure to 100 L or the O$_2$ exposure to 8,000 L at 550 K. STM image on the surface after 250 L NO$_2$ dosing at 550 K revealed an island structure composed of small agglomerates. The monoatomic step height was not expanded.

Oxidation of Pd(110) in high pressure oxygen, the oxygen uptake increased with oxygen gas phase pressure up to 50 Torr at 600 K. Above 50 Torr or at higher temperature, the
uptake became zero order of the oxygen pressure. Meantime, a two-stage mechanism was distinguished after exposure the sample for extended time. In the first step, exposure of Pd(110) to O₂ for a short period of time, the oxygen uptake rate was a function of O₂ pressure, the treatment temperature and the oxidation time. Whereas, in the second step, oxidation of Pd(110) for a sufficiently long period of time, bulk oxide was formed. The oxygen uptake rate was limited by the diffusion of oxygen in PdO phase, and did not change with the gas phase pressure. Although the oxygen diffusion in the second step occurred at a relatively lower rate as comparing to that in the first step, both diffusions obeyed the Mott-Cabrera parabolic law that described that the oxygen uptake was proportional to the square root of time. The formation of bulk PdO was accelerated at higher temperature and higher oxygen pressure.

The surface morphology change was imaged by STM. After 1 Torr O₂ exposure, an island structure appeared on the surface. The step height was increased by 0.1-0.3 Å due to the expansion of Pd crystalline structure to accommodate the diffused oxygen atoms. Oxide agglomerates nucleated after 5-25 Torr O₂ oxidation. The elongated agglomerates with aspect ratio 2.5:1-4.0:1 grew parallel to one another along <1\bar{1}0> direction. The agglomerate size did not change much with the pressure increase up to 25 Torr. Bulk PdO was formed which was characterized by the complete fading out of Pd metallic spots (so the average thickness of the PdO layer should be above 2 ML), the O/Pd atomic ratio around 0.3-0.7 and the amorphous surface structure composed of semi-spherical agglomerates. The size of the semi-spherical agglomerates increased from around 3 nm to 4 nm with pressure increase from 50 Torr to 150 Torr. In consistent with the STM images, the surface area measured by integrating the STM data showed a continuously
increase during the oxidation. The surface expanded 30-40% after the bulk PdO formation. The surface was also roughened with increasing the oxidation time and the treatment temperature.
REFERENCES


[29] Cabrera, N., Mott, N.F., Repts. on Prog. in Phys. 12, 163 (1949).


<table>
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<th>Reaction condition</th>
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<th>Stable oxygen uptake</th>
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<td>1 Torr O₂, 600 K, 10 min</td>
<td>9 ML</td>
<td>15 ML</td>
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<tr>
<td>10 Torr O₂, 600 K, 10 min</td>
<td>12 ML</td>
<td>20 ML</td>
</tr>
<tr>
<td>1 Torr O₂, 780 K, 1 min</td>
<td>21 ML</td>
<td>36 ML</td>
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Figure 4.1 Clean Pd(110) surface (a) LEED pattern (73eV) (b) STM image, sample bias was 0.7 V and tunnelling current was 1 nA.
Figure 4.2  Pd(110)-c(2×4)-O surface (a) LEED pattern (73eV) (b) Schematic of the LEED pattern
Figure 4.3  STM images on Pd(110)-c(2×4)-O surface (a) large scale image (b) high-resolution image. Point “a” in (a) marks the grain boundaries and defects. The rectangle in (b) displays a unit cell structure. Sample bias was 0.7 V and tunnelling current was 1 nA.
Figure 4.4  TPD spectra obtained on Pd(110) surface following (a) 12 L O$_2$ adsorption at 550 K (b) 12 L NO$_2$ adsorption at 550 K
Figure 4.5  (a) LEED pattern obtained by 12 L NO$_2$ adsorption at 550 K (73 eV) (b) schematic LEED pattern for (a)
Figure 4.6  STM images obtained after exposure Pd(110) to (a) 12 L NO₂ at 550 K (b) 250 L NO₂ at 550 K. Sample bias was 0.7 V and tunnelling current was 1 nA.
Figure 4.7  Oxygen uptakes after oxidation of Pd(110) in different O$_2$ pressures (1-150 Torr) at 600 K, 650 K and 700 K for 10 min.
Figure 4.8 Oxygen uptakes as a function of time of oxygen exposure under various reaction conditions. Step I. 1-1 Torr, 600 K; 2-10 Torr, 600 K; 3-50 Torr, 600 K; 4-1 Torr, 650 K; 5-1 Torr, 700 K; 6-1 Torr, 750 K; 7-1 Torr, 780 K
(a) Oxygen uptake (ML) vs. Time of reaction $t^{1/2}$ (min $^{1/2}$)

(b) Oxygen uptake (ML) vs. Time of oxygen exposure $t^{1/2}$ (min $^{1/2}$)
Figure 4.9  Oxygen uptakes as a function of time of oxygen exposure under various reaction conditions. Transition from Step-I to Step-II. (a) 10 Torr and 50 Torr oxygen at 600K  (b) 1 Torr oxygen at 700K, 750K, and 780K.
(a) 

(b)
Figure 4.10  Oxygen uptakes as a function of time of oxygen exposure under various reaction conditions. Step-II. (a) 10 Torr and 50 Torr oxygen at 600 K (b) 1 Torr oxygen at 700 K, 750 K, and 780 K.
Figure 4.11 STM images obtained after exposure Pd(110) at 600 K for 10min to different oxygen pressures (a)1 Torr (b) 5 Torr (c) 10 Torr (d) 25 Torr (e) 50 Torr (f) 100 Torr (g) 150 Torr. Sample bias was 0.1-1 V, tunnelling current was 0.1-1 nA.
Figure 4.12  Surface area increase as a function of oxygen pressure after exposure Pd(110) at 600 K for 10 min
Figure 4.13  STM images obtained after exposure Pd(110) at 600K to 10 Torr O\textsubscript{2} for different durations (a) 1 min (b) 30 min (c) 60 min. Sample bias was 0.1-1 V, tunnelling current was 0.1-1 nA.
Figure 4.14  Surface area increase as a function of oxidation time determined after exposure Pd(110) to 10 Torr oxygen at 600 K
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Chapter

5 Oxidation of Pd(100) in High Pressure Dioxygen
Abstract

Oxidation of Pd(100) in high pressure O₂ (1-150 Torr) at temperatures between 600-780 K was characterized by Scanning Tunneling Microscopy (STM), Auger-electron Spectroscopy (AES), Temperature Programmed Desorption (TPD) and Low Energy Electron Diffraction (LEED). The oxidation of Pd(100) was rate-limited by the diffusion of oxygen through a thin oxide layer and subsequently the diffusion through a bulk PdO. At 600 K, the diffusion of oxygen in the thin oxide layer occurred with the diffusion coefficient of $1.41 \times 10^{-16}$ cm² s⁻¹, and the oxygen diffusion coefficient in the bulk PdO was $4.70 \times 10^{-18}$ cm² s⁻¹. The diffusion rates were temperature-activated. The activation energies were 77 kJ mol⁻¹ and 126 kJ mol⁻¹ in the thin oxide layer and in the bulk oxide, respectively. Both diffusion processes followed the Mott-Cabrera parabolic law. The surface morphology of Pd(100) changed as a function of oxidation conditions. Islands were formed by exposure to 1 Torr O₂ at 600 K for 10 min. The inter-planar spacing for the first two surface layers was expanded by approximately 10% due to the oxygen diffusion into Pd near surface region. Semi-spherical oxide agglomerates along the steps nucleated and grew on Pd(100) surface after oxidation in 5-25 Torr O₂ at 600 K. The formation of bulk oxide was characterized by a roughened amorphous “cauliflower-like” surface structure aggregating semi-spherical agglomerates approximately 2.8-3.5 nm in size. The surface roughening was accelerated by increasing the oxygen pressure. The surface area increased about 118% after exposure to 150 Torr O₂ at 600 K for 60 min.
5.1 Introduction

The practical importance of catalytic methane combustion on palladium metals has spurred many investigations on this system over the years. Palladium has been considered as the best catalyst for complete CH₄ combustion because of the highest turnover rate [1]. During the reaction, palladium can exist as either metallic Pd or palladium oxide depending on the combustion temperature and the oxygen partial pressure. In air at atmospheric pressure, PdO is the active phase up to 1052 K [2-4]. This unusual behavior suggests that the oxidation of Pd surface might play an important role in determination of the catalytic activity. Therefore we have initiated a project aimed at characterizing the oxidation mechanism of Pd surfaces in a condition close to realistic CH₄ combustion environment. The interaction of oxygen with a Pd single crystal surface typically the surface morphology transformation after an exposure to oxygen in the pressure range of 1-150 Torr and temperature between 600-900 K is investigated using Scanning Tunneling Microscopy (STM) along with Temperature Programmed Desorption (TPD), Auger-electron Spectroscopy (AES), and Low Electron Energy Diffraction (LEED). As compared to the previous studies on Pd oxidation in low oxygen pressures (typically < 10⁻⁶ Torr) and/or at low temperatures for instance [5-17] and references therein, this research should be of more interest for industrial applications. In this paper the oxidation of Pd(100) is discussed and the results are compared with previous work obtained on Pd(111) and Pd(110) in our group [18, 19].

Prior work has suggested that in high vacuum conditions oxygen dissociatively adsorbs on Pd(100) at above 125 K [20] with an initial sticking coefficient of 0.1 ± 20% [16] or
0.4 [17, 21]. Four surface structures induced by atomic oxygen adsorption are observed using LEED with increased oxygen coverages including p(2×2), c(2×2), (5×5) and ($\sqrt{5} \times \sqrt{5}$)R27° [11, 16, 22-26]. The p(2×2) phase is observed for coverages ranging from 0.05 ML to 0.25 ML. Upon increasing the oxygen exposure, p(2×2) could be gradually replaced by c(2×2) with the maximum coverage of 0.5 ML. Both p(2×2) and c(2×2) are attributed to simple atomic oxygen overlayers with oxygen atoms suggested to reside in the four-fold hollow sites by STM [11] and Electron Energy Loss Spectroscopy (EELS) [17, 27]. A metastable c(2×2) structure could be formed without an intermediate p(2×2) structure under conditions of slow diffusion combined with rapid oxygen adsorption, for example at low substrate temperature of 150-180 K and at high oxygen impingement rate [28]. The oxygen-induced structure reconstruction of the Pd(100) surface occurs at higher coverage at the expense of c(2×2). Studies with LEED and TPD suggest that the two reconstructed structures (5×5) and ($\sqrt{5} \times \sqrt{5}$)R27° with ideal coverages of 0.64 ML and 0.80 ML are formed involving an activated process [28], since the formation of (5×5) structure requires temperature above 400 K [22] or 473 K [16], and the ($\sqrt{5} \times \sqrt{5}$)R27° structure would not be formed at temperature below 573 K [16]. Increase the oxygen exposure could help to lower the surface reconstruction barrier. After sufficient O₂ exposure, Zheng and Altman [11] were able to observed the (5×5) structure at 335 K and the ($\sqrt{5} \times \sqrt{5}$)R27° at 400 K. The surface structures of (5×5) and ($\sqrt{5} \times \sqrt{5}$)R27° are suggested to resemble to the PdO(110) [16, 28] and the PdO(001) [11, 25] planes on top of a distorted Pd(100) surface. While a most recent Core-Level Spectroscopy (CLS)
study assigned the ($\sqrt{5} \times \sqrt{5}$)R27° structure to a strained PdO(101) two-dimensional layer [26].

Differing from the previous oxidation work in low oxygen pressure, Pd(100) was oxidized in 1-150 Torr O₂ at 600-780 K for 1-180 min in this study. It will be shown that oxidation of Pd(100) in high pressure oxygen is qualitatively similar to the oxidation of Pd(111) and Pd(110). The amount of oxygen uptake measured under the same oxidation conditions is approximately inversely proportional to the Pd atom densities on the three surfaces. The oxidation of Pd(100) is rate-limited by the diffusion of oxygen through a thin oxide layer and subsequently the diffusion through a bulk PdO. The surface morphology of Pd(100) changes as a function of oxidation conditions. The oxidized Pd(100) surface was roughened and formed an amorphous “cauliflower-like” structure by aggregating semi-spherical agglomerates. This roughened oxide surface observed after oxidation of Pd in high pressure O₂ may represent the surface states in realistic CH₄ combustion reaction.

5.2 Experimental Methods

The experiments were carried out in a specially designed system consisting of three stainless steel chambers: an Ultra-High Vacuum (UHV) analysis chamber, a UHV STM chamber and a high-pressure reaction cell. The analysis chamber housed facilities for AES, LEED and TPD. The STM chamber accommodated an ambient-temperature UHV STM (RHK. Inc). The base pressure after bake out in UHV chambers was $5 \times 10^{-10}$ Torr and in the high-pressure reactor was $2 \times 10^{-8}$ Torr (1 Torr = 133.3 Pa).
The sample was a 1.0 mm thick, 8.5 mm diameter single crystal Pd(100) (Princeton Scientific Corp.) with misalignment < 0.5°. The single crystal was mounted on a standard RHK sample holder. The temperature was measured by a chromel-alumel thermocouple spot-welded onto the side of the sample. In the analyzing chamber, the sample was heated by electron-bombardment from the rear, and in the reaction cell, the sample was heated by an IR lamp.

The TPD spectra were collected by means of a RGA-200 mass-spectrometer at a constant heating rate of 5 K s⁻¹. The coverage was calculated by integrating area under a TPD peak and measured in monolayers (ML). Calibration of the coverage was based on assuming that a saturated Pd(100) surface with a \((\sqrt{5} \times \sqrt{5})_{\text{R}27}\) structure has an ideal 0.8 ML oxygen coverage [11].

The sample cleaning procedure consisted of repeating cycles of Ar⁺ sputtering at room and elevated temperatures, flashing up to 1000 K, exposure to O₂ and NO₂ followed by annealing at 1000 K for 60 seconds under UHV conditions. The sample cleanliness was checked by TPD, AES and LEED. NO₂ and O₂ were introduced into the analysis chamber through a capillary dozer.

The STM images were obtained using Pt-Ir tips electrochemically etched in NaCl/NaNO₃ (molar ratio 1:4) melt at around 400-450 °C. Sample bias with respect to the tip of 1 V and tunneling currents of 0.1-0.5 nA were applied for all images shown. Surface area increase after oxidation of the Pd(110) single crystal was determined from analysis of the STM images by taking the discrete image pixels and joining them by a series of triangles. Integration of the area of individual triangle gives the total area [19].
The following experimental protocol was used for oxidation experiments. The single crystal was heated to the desired temperature in vacuum and then oxygen was introduced. After oxidation, the sample was cooled and oxygen was pumped out simultaneously. It took less than 1 min to reduce the sample temperature to 450 K and to reach the vacuum in the reactor better than $10^{-6}$ Torr. After a treatment, the sample could be transferred into the STM and/or analysis chamber by means of a 142 cm transfer arm without contact with atmosphere.

5.3 Results

5.3.1 Oxygen adsorption on Pd(100)

Clean Pd(100) has a well-defined square LEED pattern as shown in Figure 5.1(a). The measured nearest atom spacing was $2.68 \pm 0.13 \text{ Å}$ (theoretical spacing is $2.75 \text{ Å}$). Exposure of the single crystal to 50 L O$_2$ at 400 K resulted in a surface with 0.33 ML coverage. The LEED pattern (Figure 5.1(b)) on this surface revealed common (1/2, 1/2) spots for both p(2×2) and c(2×2) phases and (1/2, 0) uniquely for p(2×2) phase. The (5×5) LEED pattern in Figure 5.1(c) was observed after an exposure of Pd(100) to 300 L O$_2$ at 500 K. And the $(\sqrt{5} \times \sqrt{5})R27^\circ$ reconstructed structure (Figure 5.1(d)) could be obtained by either 800 L O$_2$ exposure or by 12 L NO$_2$ exposure at 550 K.
5.3.2 Oxygen uptake after high pressure (1-150 Torr) O\textsubscript{2} treatment

5.3.2.1 Pressure effect

The single crystal Pd(100) was exposed to O\textsubscript{2} at elevated sample temperatures of 600, 650 and 700 K for 10 min in the O\textsubscript{2} pressure range 1-150 Torr. The oxygen uptakes after different high-pressure treatment were calculated by integrating TPD spectra and plotted as a function of O\textsubscript{2} pressure in Figure 5.2. As one can see, at 600 K the oxygen uptake increased quickly with O\textsubscript{2} pressure up to 50 Torr. The relation could be described as:

\[ N_{oxygen} \propto P_{O_2}^{0.2} \]  \hspace{1cm} (1)

Above 50 Torr, the uptake leveled off and appeared to be almost independent to the O\textsubscript{2} pressure. Raising the O\textsubscript{2} treatment temperature lowered the pressure at which the transition occurred. The oxygen uptake rate became zero order of the pressure at 650 K in O\textsubscript{2} above 5 Torr and at 700 K in O\textsubscript{2} above 1 Torr. It should be noted that the pressure independence was accompanied with the complete fading out of the Pd(100) (1\times1) LEED pattern and an O/Pd atomic ratio above 0.3 was detected with AES.

5.3.2.2 Oxidation time effect

The oxygen uptake on Pd(100) increased with the oxidation time as shown in Figure 5.3 and Figure 5.4. Figure 5.3 represents the uptakes after oxidation at 600 K in 1-150 Torr O\textsubscript{2} for various time intervals between 1-180 min, and the uptakes after oxidation in 1 Torr O\textsubscript{2} at 650-750 K are given in Figure 5.4. Clearly a two-step mechanism was distinguished in both Figures. For the sake of expression, the two steps are designated as step-I and step-II in the following context.
In step-I, for a short period of time, the oxygen uptake was linearly proportional to the square root of the time of reaction as shown in Figure 5.3(a) and 5.4(a). The time dependence of the oxygen uptake thus could be expressed by the Mott-Cabrera parabolic diffusion law [29]:

\[ N_{\text{oxygen}} = K_1 (T, P) \cdot t^{\frac{1}{2}} \]  

Here \( K_1 \) is the parabolic rate constant and as has been illustrated in the Figure 5.3(a) a function of \( O_2 \) pressure up to 50 Torr and in the Figure 5.4(a) a function of sample temperature. Note that despite the large amount of oxygen uptake on the sample for example 37 ML after oxidation in 1 Torr \( O_2 \) at 750 K for 5 min in this step, a slightly diffused Pd(100) (1×1) LEED pattern was observed on the surface, and no essential amount of oxygen (< 5%) was detected with AES.

The transition from step-I to step-II is clearly demonstrated in the Figure 5.3(b) and 5.4(b) which is characterized by a considerably dropping in the \( O_2 \) uptake rate after oxidation of Pd(100) for a sufficiently long period of time. As one can see, the moment for the transition to occur strongly depends on the \( O_2 \) pressures (Figure 5.3(b)) and the treatment temperatures (Figure 5.4(b)).

The time dependence for the \( O_2 \) uptake in the step-II as shown in Figure 5.3(c) and 5.4(c) could be well expressed as:

\[ N_{\text{oxygen}}^2 - N_{\text{oxygen}_0}^2 = K_2 (T)^2 \cdot (t - t_0) \]  

Here \( K_2 \) is the rate constant in this step, \( t_0 \) is the starting point for the transition from step-I to step-II and \( N_{\text{oxygen}_0} \) is the oxygen uptake at \( t_0 \). Apparently, \( K_2 \) was also a function
of sample temperature (Figure 5.4(c)) but not of $O_2$ pressure, since similar $K_2$ was obtained after oxidation of Pd(100) at 600 K in different $O_2$ pressures (Figure 5.3(c)). The rate expression in equation (3) suggested that the oxygen uptake in this step also obeyed the Mott-Cabrera parabolic diffusion law, except that the parabolic rate constant $K_2$ was smaller than $K_1$ in step-I.

5.3.2.3 Depth profile of oxygen in Pd(100)

Given the extremely slow diffusion of oxygen in the Pd(100) as suggested in the Figure 5.2-5.4, it is reasonable to treat the 1 mm thick Pd(100) single crystal as a semi infinite slab. The depth profile of oxygen in Pd(100) could then be simulated mathematically by solving the Fick’s second law in the $z$ (depth) dimension:

$$\frac{\partial C_O}{\partial t} = D_{O-Pd} \frac{\partial^2 C_O}{\partial z^2}$$

The boundary and initial conditions are:

$$t = 0; \quad \frac{C_O}{C_{O-0}} = 0; \quad z \geq 0;$$

$$t > 0; \quad z = 0; \quad \frac{C_O}{C_{O-0}} = 1;$$

$$t > 0; \quad \frac{C_O}{C_{O-0}} = 0; \quad z \rightarrow \infty;$$

Here, $C_O$ is the oxygen concentration along the $z$ dimension in Pd(100); $C_{O-0}$ is the surface oxygen concentration, which remains as a constant at $t > 0$. The analytical solution in terms of the dimensionless oxygen concentration is [30]:
\[
\frac{C_O}{C_{O-0}} = \text{erfc} \left( \frac{z}{2\sqrt{D_{O-Pd}} t} \right)
\]

The diffusion coefficient \(D_{O-Pd}\) was then obtained using trial-and-error method in which the numerical integration of the oxygen depth profile gave the total \(O_2\) uptake after a certain period of oxidation time \(t\). The typical diffusion coefficient at 600 K was determined to be \(1.14 \times 10^{-16}\) cm\(^2\) s\(^{-1}\) in the diffusion step-I and \(4.70 \times 10^{-18}\) cm\(^2\) s\(^{-1}\) in step-II.

The simulated oxygen distribution profile in Pd(100) along the dimensionless depth \(z/z_0\) is given in Figure 5.5. Here, \(z_0\) is the a single step height and equal to 1.94 Å on Pd(100). Figure 5.5(a) represents the oxygen distribution after oxidation in 10 Torr \(O_2\) at 600 K for 1, 5, 10, 20 and 30 min and Figure 5.5 (b) shows the oxygen depth profile after oxidation in 1 Torr \(O_2\) for 10 min at 600, 650, 700, 750 and 780 K. Clearly, the depth of oxygen diffusion into palladium increases with the extension of the \(O_2\) exposure time as well as the enhancement in the exposure temperature.

The activation energies for the two diffusion processes step-I and step-II are derived from the Arrhenius plot of \(D_{O-Pd}\) with varying temperatures in the range of 600-780 K as shown in Figure 5.6(a). The higher activation energy of 126 kJ mol\(^{-1}\) in step-II as comparing to the 77 kJ mol\(^{-1}\) in the step-I suggested the formation of a higher oxygen diffusion barrier after oxidation for extended time.
5.3.3 Comparison the oxidation of Pd(100) with the oxidation of Pd(111) and Pd(110)

Figure 5.6 and Table 5.1 provide the comparison of the activation energies for oxygen diffusion in the three lowest index Pd single crystals. The similar activation energies were determined on the three single crystals for both the step-I and the step-II.

The comparison of the O$_2$ uptakes on Pd(111), Pd(100) and Pd(110) after oxidation at 600 K in 1-150 Torr O$_2$ for 10 min is provided in Figure 5.7. It was shown that the oxidation of Pd(100) shares the same trend as Pd(110) and Pd(111) oxidation. The uptake rate increased with the oxygen pressure and then declined at around 50 Torr. The amount of uptake on the three surfaces increased in the order from Pd(111), Pd(100) to Pd(110) and was approximately inversely proportional to the Pd surface atom densities. The Pd atom density on Pd(111) is $1.53 \times 10^{15}$ atom cm$^{-2}$; on Pd(100) is $1.32 \times 10^{15}$ atom cm$^{-2}$; and on Pd(110) is $0.94 \times 10^{15}$ atom cm$^{-2}$. For instance, in 50 Torr of O$_2$ the uptakes on the three surfaces were 16, 21 and 26 ML (1:1.3:1.6), and the inverse proportion for the Pd surface densities was 1:1.2:1.6. The highest uptake was observed on Pd(110), which has the most open surface structure.

5.3.4 Alternating oxidation procedure

Exposure of Pd(100) to 1 Torr O$_2$ at temperatures between 600 and 780 K for short period of time followed by quenching in vacuum resulted in only slightly diffused Pd(100) (1×1) LEED pattern. It was found however that a weakened ($\sqrt{5} \times \sqrt{5}$)R27° LEED pattern was observed when the sample was quenched in O$_2$ pressure to below 400 K after 1 Torr O$_2$ oxidation at 600 K for 10 min or at 750 K for
5 min. In addition AES also detected the oxygen signal, and the O/Pd atomic ratio was around 0.09.

5.3.5 Surface morphology after high-pressure (1-150 Torr) O₂ treatment

5.3.5.1 O₂ pressure effect

Structural changes on the Pd(100) surface after oxidizing the single crystal was studied by Scanning Tunneling Microscopy. Figure 5.8 shows the set of typical STM images obtained after treatments in 1, 5, 10, 25, 50, 100 and 150 Torr O₂ at 600 K for 10 min. Clearly, the single crystal surface structure changed with the increase of the O₂ pressure and the surface area estimated by STM image analysis experienced three major increases as the O₂ pressure increased stepwisely.

Exposure of Pd(100) to 1 Torr O₂ at 600 K for 10 min, a number of different surface features (Figure 5.8(a)) were revealed as comparing to the clean single crystal surface. First, the terraces, which were approximately 250-300 Å in width on the clean Pd(100) surface, narrowed up to 80-120 Å after the 1 Torr oxygen treatment. Some extremely narrowed terraces with the width of only 10-40 Å were also observable in the image as pointed out by the dashed arrows. Second, most of the terraces shown in the image did not have a uniform width; a typical terrace was marked out by “a”. Third, the step edges became curved, no longer straight as on the clean Pd(100) surface. Fourth, the terraces were separated by steps with the depth being mostly in the range of 2.1 ± 0.2 Å. This value was bigger than that on a clean Pd(100) surface of 1.94 Å. The step height could however also been measured to be about 2.5-2.8 Å, especially between a wide and a narrow terraces. Occasionally, the step with 3.9-4.6 Å in height could be measured
corresponding to the appearance of double-atomic steps. Fifth, small pits with the mean size of 7 Å and the depth of 2.2 ± 0.2 Å appeared. These pits normally located along the step edges, but could be observed also on a wide terrace. Finally, a slightly diffused (1×1) LEED pattern was observed after the treatment; moreover AES did not detect any oxygen trace despite the oxygen uptake of 10 ML (Figure 5.2).

Raising the O₂ pressure to 5 Torr induces the nucleation and growth of semi-spherical agglomerates as shown in Figure 5.8(b). Atomic step became indistinguishable after the 5 Torr exposure. Although the shape of the agglomerates was not quite clear since the edges were blurred and some of the agglomerates looked as if they were attached to another one in the step direction, the size of the agglomerates could be estimated to be about 2.0-4.0 nm. These agglomerates tended to have a general orientation parallel along the steps. Again, oxygen was not detected by AES after the 5 Torr O₂ treatment. LEED revealed a diffused Pd(111) (1×1) pattern. Zooming into the individual agglomerates revealed no evidence of atomic scale features.

The STM images obtained after exposure of Pd(100) in 10 Torr and 25 Torr O₂ at 600 K for 10 min as shown in Figure 5.8(c) and (d) again reveals an agglomerate surface structure; although the agglomerates as compared with those grown in 5 Torr O₂, had a more clear and definite shape with the relatively uniform size of 4.1 ± 0.5 nm after 10 Torr treatment and 3.9 ± 0.4 nm after 25 Torr treatment. The agglomerates grown under the two conditions were visible to still orient slightly angled to the steps. Noteworthy that only very weak Pd(100) (1×1) LEED pattern was observed on the surface after the 25 Torr O₂ treatment; and AES detected oxygen with O/Pd atomic ratio of 10.2%.
The formation of bulk PdO starts after exposure of the Pd(100) to 50-150 Torr O$_2$ as shown in Figure 5.8(e) through (g). The growing PdO formed a number of semi-spherical agglomerates. And these agglomerates tended to aggregate together to form a large “cauliflower-like” superstructure with no preferred orientations. This tendency of aggregation was more apparent on the surface after 100 Torr treatment. The size of the semi-spherical agglomerates changed slightly with the pressures, being $2.8 \pm 0.5$ nm at 50 Torr, $3.2 \pm 0.4$ nm at 100 Torr and $3.5 \pm 0.5$ nm at 150 Torr, respectively. According to AES, the atomic ratio between O and Pd was 0.29 and 0.39 after 50 and 150 torr of O$_2$.

The increase in the Pd(100) surface area after 1-150 Torr O$_2$ treatments at 600 K for 10 min is estimated by integrating the STM data and illustrated in Figure 5.9. As expected from the surface morphologies shown in Figure 5.8, the surface area did not increase linearly with the O$_2$ pressure, but rather fell into three distinct regions at low (P$_{O_2}$ around 1 Torr), intermediate (P$_{O_2}$ in the range of 5-25 Torr) and high pressures (P$_{O_2}$ > 50 Torr). Surface area increased about 2% after oxidation in the low-pressure regime. A 10-25% expansion of the surface was measured after a treatment in the intermediate-pressure region. And a 40-55% area increase was determined for the high-pressure regime. The increase in the Pd(100) surface area by oxygen treatment was qualitatively similar to those on Pd(111) and Pd(110) [18].

5.3.5.2 Oxidation time effect

It is found that extension of the oxidation time could also lead to the roughening of the surface as shown in Figure 5.10 after exposing a Pd(100) surface to 10 Torr O$_2$ at 600 K for 1-60 min. The STM image obtained after 1 min O$_2$ exposure (Figure 5.10(a)) reveals
a surface structure similar to that on a clean Pd(100), except that the terrace is narrowed up to 100-150 Å in width and the step height is expanded to be in the range of 2.05 ± 0.2 Å. As comparing to the structure observed after 10 min treatment (Figure 5.8(c)), the (100) surface exposed to 10 Torr O$_2$ for 30 min does not undergo significant structural changes (Figure 5.10(b)). The surface was covered with semi-spherical agglomerates 4.3 ± 0.3 Å in size, and these agglomerates tended to orient along the steps. After 60 min treatment in 10 Torr O$_2$, the Pd(100) surface appeared a “cauliflower-like” superstructure which was composed of PdO agglomerates around 3.5 ± 0.4 Å in size as shown in Figure 5.10(c); although judging from the STM image, the structure still showed a slightly preferential growth orientation along the step direction.

The surface area increase on Pd(100) after the 10 Torr O$_2$ treatment shown in Figure 5.12(a) was consistent with the three-step surface reconstruction process. The surface area increased less than 10% after 1 min treatment; a 15-25% area increase was determined on the surface after 10-30 min treatments; once the bulk oxide was formed, the surface area increased drastically to 47% after the O$_2$ treatment for 60 min.

Increasing the O$_2$ pressure could accelerate the surface roughening process as shown in Figure 5.11 and Figure 5.12(b). A surface area increase of 118% was measured after oxidation of Pd(100) in 150 Torr O$_2$ at 600 K for 60 min.
5.4 Discussion

5.4.1 Diffusion processes

The results in Figure 5.3 and 5.4 suggested that the oxidation of a single crystal Pd(100) was rate-limited by two diffusion processes, where the diffusion in step-I occurred at a significantly higher rate than that in step-II with a diffusion coefficient about two-orders of magnitude higher.

It was determined in this work that the oxygen diffusion coefficient at 600 K in step-II was about $4.70 \times 10^{-18}$ cm$^2$ s$^{-1}$ on an oxidized Pd(100) and about $6.82 \times 10^{-18}$ cm$^2$ s$^{-1}$ on an oxidized Pd(110). This value agreed reasonably well with the diffusion coefficient of oxygen in a palladium oxide reported by Au-Yeung et al. [31] of $2.86 \times 10^{-18}$ cm$^2$ s$^{-1}$. This fact is an indication that after oxidation of Pd single crystals for sufficiently long time in high-pressure of O$_2$, a bulk PdO is formed. The surface of the bulk oxide layer is saturated with oxygen, so the diffusion rate is independent to the O$_2$ gas phase pressure (Figure 5.2 and Figure 5.3(c)). In addition, the bulk oxide layer provides a strong oxygen diffusion barrier, in which the oxygen diffusion proceeds at a much lower rate (Figure 5.3(b) and Figure 5.4(b)). It is recognized however that, there exists an un-negligible discrepancy between the activation energies reported in these two work, 126 kJ mol$^{-1}$ in the present work and 89 kJ mol$^{-1}$ reported by Au-Yeung et al. [31]. The possible reason for this discrepancy could be due to the different oxide agglomerate size observed after oxidation of Pd single crystals. It has been suggested that the activation energy for oxygen diffusion in PdO varies with the oxide agglomerate size with the larger agglomerates present the lower activation energy [31]. Indeed, increasing the PdO
agglomerate size would result in the weakening of Pd-O bonds [32], enabling diffusion to occur more rapidly.

The oxygen diffusion coefficient in step-I was also determined in the present work to be about $1.14 \times 10^{-16}$ cm$^2$ s$^{-1}$ at 600 K with an activation energy of 77 kJ mol$^{-1}$. It is unlikely that this process is the oxygen atoms diffusing through a metallic palladium, since the diffusion coefficient for oxygen in Pd metal is in a range of $10^{-10}$-10$^{-12}$ cm$^2$ s$^{-1}$ at 600 K [33, 34]. Note that in reference [33], the diffusion coefficient was converted to the unit of cm$^2$ s$^{-1}$ from ML s$^{-1}$ for comparison. The surface is not in a bulk oxide state either, since in this step the Pd(100) (1×1) pattern for the metal substrate was still observable; moreover, AES detected O concentration on the surface less than 0.05. The thickness of the surface layer should average around 2.5 ML since the mean free path of electron in Pd metal at 63 eV, the beam energy used for LEED, is about 0.5 nm. To interpret this surface layer, several surface states could be imagined. First, the surface could be uniformly covered with a thin surface oxide layer after oxidation for a short period of time. In fact, the formation of the surface oxide was confirmed by quenching the sample pre-exposed to 1 Torr O$_2$ at 600 K for 10 min in an O$_2$ pressure from the reaction temperature to below 400 K before transferring to the analysis chamber as described in the result section, although the oxide layer disappeared either due to thermal decomposition or dissolution into Pd bulk if quenching in vacuum. This surface oxide is distinct from Pd metal but similar to the PdO(001). The formation of the surface oxide layer was also observed on Pd(111) and Pd(110) by NO$_2$ adsorption or by quenching in O$_2$ pressure after an oxygen pre-exposure, except that it has a complex structure not similar to the PdO as in the Pd(100) case [10, 13, 18]. Second, patches of stoichiometric
PdO could be formed on the surface. PdO nucleates and grows starting from the sites of defects, grain boundaries and step edges, which have a higher oxygen sticking coefficient. Although it has been suggested that metallic Pd and PdO cannot coexist at equilibrium, and Pd is insoluble in PdO [35], given a slow process of oxidation, Pd and PdO might coexist for a short period of time when metallic Pd is exposed in an oxygen environment favorable for the formation of oxide. TEM studies by Datye et al. [36] suggested patches of Pd metal was coexisting with a polycrystalline PdO during oxidation upon cooling down a Pd/Al₂O₃ catalyst from 1173 K to room temperature (RT) in air at 5 K min⁻¹. Third, stoichiometric PdO clusters could uniformly nucleate on the single crystal surface. As a result of the lower surface tension of the oxide phase compared with the metal phase, the small PdO clusters are easily dispersed and tend to encapsulate Pd metal to form agglomerates with surface PdO and a core of metallic Pd. On the Pd(111) surface, the formation of uniformly distributed small oxide agglomerates appeared after oxidation in 10-25 Torr O₂ at 600 K for 10 min. On Pd(110), a number of elongated oxide agglomerates were observed aligning along <110> direction following the oxidation in 5-25 Torr O₂ at 600 K [18]. And on the surface of Pd(100), semi-spherical oxide agglomerates formed along the step direction after an exposure in 5-25 Torr O₂ at 600 K. Finally, a buried oxide could be formed as suggested by Over et al. [37, 38]. They found that a significant amount of oxygen (equivalent to 20 to 30 ML) was incorporated into the Ru(0001) surface without surface oxide formation after NO₂ dosing.

As the various oxidation states discussed so far (surface oxide, patches of oxide, metal-core-oxide and buried oxide), which dominates the surface in diffusion step-I is not clear
yet. The possibility of oxide patches or buried oxide formation is relatively low, as this oxide layer would not effectively passivate the oxygen diffusion. It might however, coexist with other oxide species. Unfortunately, since we performed ex-situ study, it is impossible for us to define the nature of the surface oxygen species. A careful in-situ study is required to answer this question unambiguously. Clearly, the oxide layer formed on the surface in the step-I should have weakened Pd-O bonds to enable the rapid oxygen diffusion. In addition the oxide layer should be thin to allow the electron to penetrate when detected with LEED and AES.

Note that a large amount of oxygen is incorporated into palladium in this step, which is far beyond the accommodation in the thin oxide layer on the surface. This could be understood in terms of the diffusion of oxygen atoms into metallic Pd near surface region as suggested by Campbell et al. [39], a solid solution of oxygen in palladium is formed. Since the diffusion in Pd metal occurs at a much higher rate with the diffusion coefficient almost four-orders magnitude higher than the oxygen diffusion through the thin oxide layer, it does not appear to be the rate-limiting step.

5.4.2 Surface morphology changes after 1 Torr O₂ exposure at 600 K for 10 min

A number of different surface features, as compared with the clean Pd(100), were revealed after an exposure to 1 Torr O₂ at 600 K for 10 min. The fact that the terrace was narrowed and the step edge was curved is an indication that islands with the same depth as monoatomic step height were growing either on top of a wide terrace or out of the original step edges. The growth of the islands as suggested by Zheng and Altman [11] started once the original terraces were fully covered by an adsorbed layer of oxygen. The
non-uniform width of the terraces could also be attributed to the formation of islands with irregular shapes.

Oxygen diffused into the Pd near surface region during the exposure. To accommodate the interstitial oxygen atoms, the Pd crystal structure was expanded and revealed by the increase of the inter-planar spacing of the two surface layers of approximately 10% comparing to the clean Pd(100). The particular height variation measured to be about 2.5-2.8 Å might be attributed to the growth of a “new intermediate-height level” on the terraces as suggested by Zheng and Altman [11] during exposure of Pd(100) to $2 \times 10^{-7}$ Torr O$_2$ at elevated temperature of 500 K. The “new level” was proposed to lie about 0.6 Å below the original terraces [11].

Small pits about monoatomic step height in depth were observed on the (100) surface after the 1 Torr O$_2$ exposure, which indicates a lower Pd atom density on the surface after the treatment than on a clean Pd(100). The experimental result of alternating the oxidation procedure (see the result section) suggests that the $(\sqrt{5} \times \sqrt{5})R27^\circ$ surface oxide structure was formed during the 1 Torr O$_2$ exposure and preserved by cooling in an oxygen pressure. It is known that the Pd atom density in the $(\sqrt{5} \times \sqrt{5})R27^\circ$ structure is only about 80% of that of Pd(100)[11], thus the lower Pd density in the pits surface structure after the O$_2$ treatment could be attributed to that of the $(\sqrt{5} \times \sqrt{5})R27^\circ$ structure, which either decomposed or dissolved into Pd metal when the sample was quenched in vacuum. The similar holes structure was previously reported on a Pd(111) surface [7, 18, 40].
5.4.3 Comparison of Pd single crystal oxidation

The oxidation of the three lowest index Pd single crystals: Pd(111), Pd(100) and Pd(110) shares many similarities. Initial exposure of the three surfaces at room or elevated temperatures to O$_2$ in the pressure range of $10^{-8}$ Torr leads to the dissociative oxygen adsorption. As the oxygen uptake increases by NO$_2$ or high pressure O$_2$ exposure, a metastable surface oxide is formed characterized by a complex LEED pattern distinct from that of PdO or the original metallic facet on the (111) and (110) surfaces, but similar to PdO(001) on the (100) surface. Oxidation of Pd single crystal surfaces in O$_2$ pressure 1-150 Torr at temperature 600-800 K, the oxygen uptake is found to increase as the pressure rises from 1-50 Torr at 600 K and then levels off. The diffusion of oxygen into Pd near surface region leads to the expansion of the Pd crystal structure; the inter-planar spacing between the two surface layers is increased by 0.1-0.4 Å comparing to the step heights on clean Pd single crystals. Bulk PdO starts to form when a critical oxygen concentration is reached in the near surface region. Once the oxide is formed, the single crystal surfaces reveals an amorphous “cauliflower-like” structure composed of semi-spherical agglomerates 2-4 nm in size, and the oxidation rate is limited by the diffusion of oxygen through the oxide layer, which is well described by the Mott-Cabrera parabolic diffusion law. Similar activation energies for the diffusion of oxygen through the bulk PdO are determined on the three oxidized Pd single crystals. This fact again suggests the same oxide structure is formed irrespective to the original single crystal orientations. The oxygen diffusion in the Pd bulk region is populated by O$_2$ exposure at high temperatures, for example in 1 Torr O$_2$ at above 820 K. There are, however, also some differences between the oxidation of the (111), (100) and (110) surfaces. First, The (100) and (110)
surfaces are more reactive towards O\textsubscript{2} than Pd(111). The maximum coverage of 0.8 ML on Pd(100) and 1.8 ML on Pd(110) could be achieved by both O\textsubscript{2} and NO\textsubscript{2} dosing; but on Pd(111), the maximum coverage of 2.4 ML was only attainable after NO\textsubscript{2} exposure. Second, oxidation in high pressure O\textsubscript{2} (1-150 Torr), the open surface structure of Pd(110) allows a higher atomic oxygen diffusion rate from the surface to the bulk than can be obtained on Pd(111) and Pd(100). The oxygen uptake is approximately inversely proportional to the atomic palladium densities on the three surfaces. A direct consequence of the fast diffusion is that the formation of PdO proceeds at higher oxygen concentration on Pd(110), which results in the oxide agglomerates with smaller size grown on the oxidized Pd(110). Finally, the densely packed Pd(111) surface needs more expansion than Pd(100) and Pd(110) during the formation of PdO. This explains a 87% surface area increase on Pd(111) compared to the 49% on Pd(100) (Figure 5.9) and 30% on Pd(110) after oxidation in 100 Torr O\textsubscript{2} at 600 K for 10 min.

5.5 Summary

Exposure of Pd(100) to 50-800 L of O\textsubscript{2} at elevated temperatures of 400-550 K resulted in the dissociative adsorption of O\textsubscript{2}, which was revealed by the p(2×2) and c(2×2) LEED patterns, and further the formation of (5×5) and (\sqrt{5}×\sqrt{5})R27° reconstructed surface oxide structures. Oxidation of Pd(100) in 1-150 Torr O\textsubscript{2} at 600-780 K for 1-180 min, the oxygen uptake increased with the O\textsubscript{2} pressure up to 50 Torr at 600 K and then leveled off. Oxygen diffused into Pd near surface region during the exposure. Once a critical concentration of oxygen was reached in the near surface region, bulk PdO was formed and characterized by the fading out of Pd(100) (1×1) LEED pattern and the O/Pd atomic
ratio above 0.3 detected with AES. The oxidation was rate-limited by the diffusion of oxygen through a thin oxide layer and subsequently the diffusion through bulk PdO. The diffusion of oxygen in the thin oxide layer occurred at a much higher rate with a diffusion coefficient $D_{O-Pd}$ of $1.41 \times 10^{-16}$ cm$^2$ s$^{-1}$, which was about two orders of magnitude higher than that for the diffusion in the bulk PdO of $4.70 \times 10^{-18}$ cm$^2$ s$^{-1}$ at 600 K. The diffusion rates were temperature-activated. The activation energies were 77 kJ mol$^{-1}$ and 126 kJ mol$^{-1}$ in the thin oxide layer and in the bulk oxide, respectively. Both diffusion processes followed the Mott-Cabrera parabolic law, which described the oxygen uptake proportional to the square root of the oxygen exposure time. The surface morphology of Pd(100) changed as a function of oxidation conditions. Exposure to 1 Torr O$_2$ led to the growth of islands on the terraces. The inter-planar spacing for the first two surface layers was expanded by 0.1-0.4 Å. Semi-spherical oxide agglomerates along the steps nucleated and grew on Pd(100) surface after oxidation in 5-25 Torr O$_2$ at 600 K. The formation of bulk oxide was characterized by a roughened amorphous “cauliflower-like” surface structure, which was composed of semi-spherical agglomerates approximately 2.8-3.5 nm in size. The surface roughening was accelerated by increase the oxygen pressure. The surface area increased about 118% after exposure to 150 Torr O$_2$ at 600 K for 60 min.

In conclusion, the oxidation of the three Pd single crystals: Pd(111), Pd(100) and Pd(110) is qualitatively similar. Palladium oxide does not grow epitaxially on the surface of the three single crystals and reveals a similar amorphous oxide surface structure.
REFERENCES


Table 5.1  Activation energies for oxygen diffusion in Pd single crystals: Pd(111), Pd(100) and Pd(110) in the temperature range of 600-820 K

<table>
<thead>
<tr>
<th>Pd single crystals</th>
<th>Activation energy in step-I (kJ mol(^{-1}))</th>
<th>Activation energy in step-II (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(111)</td>
<td>-82</td>
<td>/</td>
</tr>
<tr>
<td>Pd(100)</td>
<td>-77</td>
<td>-126</td>
</tr>
<tr>
<td>Pd(110)</td>
<td>-75</td>
<td>-118</td>
</tr>
</tbody>
</table>
Figure 5.1 LEED pattern (58 eV) on Pd(100) surface
(a) clean Pd(100); (b) p(2×2) and c(2×2); (c) (5×5); (d) (\(\sqrt{5} \times \sqrt{5}\))R27°
Figure 5.2 Oxygen uptakes after oxidation of Pd(100) in 1-150 Torr O₂ at 600, 650 and 700 K for 10 min
Oxygen uptake (ML) vs. Time of oxygen exposure $t^{1/2}$ (min$^{1/2}$)

(a) Graph showing oxygen uptake at different pressures and temperatures.

(b) Graph showing oxygen uptake at 600 K and different pressures.
Figure 5.3  Oxygen uptake as a function of time of oxygen exposure. Pd(100) was exposed at 600 K to 1-150 Torr O₂ for 1-180 min (a) Step-I. 1-1 Torr; 2-5 Torr; 3-10 Torr; 4-25 Torr; 5-50 Torr; 6-100 Torr; 7-150 Torr (b) the transition from step-I to step-II (c) Step-II. 1-5 Torr; 2-10 Torr; 3-25 Torr; 4-50 Torr; 5-100 Torr; 6-150 Torr
Oxygen uptake (ML)

Time of oxygen exposure $t^{1/2}$ (min $^{1/2}$)

(a)

Oxygen uptake (ML)

Time of oxygen exposure $t^{1/2}$ (min $^{1/2}$)

(b)
Figure 5.4  Oxygen uptake as a function of time of oxygen exposure. Pd(100) was exposed at 600-750 K in 1 Torr O$_2$ for 1-180 min (a) Step-I. (b) the transition from step-I to step-II. In (a) and (b) 1-600 K; 2-650 K; 3-700 K; 4-750 K (c) Step-II. 1-650 K; 2-700 K; 3-750 K
(a) 10 Torr O$_2$, 600 K

(b) 1 Torr O$_2$, 10 min
Figure 5.5  Oxygen depth profile in Pd(100) (a) after oxidation in 10 Torr O$_2$, at 600 K for 1, 5, 10, 20, 30 min (b) after oxidation in 1 Torr O$_2$, for 10 min at 600, 650, 700, 750, 780 K
\begin{align*}
\text{Temperature } T^{-1}/K^{-1} & \\
\ln(D_{O,Pd}) \ln(cm^2 s^{-1}) & \\
E & = 77 \text{ kJ mol}^{-1} \\
E & = 126 \text{ kJ mol}^{-1}
\end{align*}

\begin{align*}
\text{Temperature } T^{-1}/K^{-1} & \\
\ln(D_{O,Pd}) \ln(cm^2 s^{-1}) & \\
E & = 82 \text{ kJ mol}^{-1}
\end{align*}
Figure 5.6  Arrhenius plot of oxygen diffusion coefficients vs. oxidation temperatures from 600-780 K to determine oxygen diffusion activation energies in Pd single crystals (a) Pd(100) (b) Pd(111) (c) Pd(10). In the Figure, curve 1-step-I ; curve 2-step-II.
Figure 5.7  Oxygen uptakes after oxidation of Pd(111), Pd(110) and Pd(100) in 1-150 Torr O$_2$ at 600 K for 10 min
Figure 5.8 STM images obtained on the surface of Pd(100) after exposure to 1-150 Torr O$_2$ at 600 K for 10 min. (a) 1 Torr O$_2$; (b) 5 Torr O$_2$; (c) 10 Torr O$_2$; (d) 25 Torr O$_2$; (e) 50 Torr O$_2$; (f) 100 Torr O$_2$; (g) 150 Torr O$_2$. Images were scanned with bias voltage 1 V, and tunnelling current 0.3 nA. The
dashed arrows pointed to the narrow terraces. The dotted arrow pointed to
the step orientation. The terrace in (a) with the mark “a” had a non-
uniform width from the upper-left corner to the lower-right corner.
Figure 5.9  Surface area increase as a function of oxygen pressure after exposure Pd(110) to 1-150 Torr O₂ at 600 K for 10 min.
Figure 5.10  STM images obtained on the surface of Pd(100) after exposure to 10 Torr O₂ at 600 K for 1-60 min (a) 1 min; (b) 30 min; (c) 60 min. Images were scanned with bias voltage 1 V, and tunnelling current 0.3 nA. The dotted arrow pointed to the step orientation.
Figure 5.11  STM images obtained on the surface of Pd(100) after exposure to 150 Torr O$_2$ at 600 K for 1-60 min (a) 1 min; (b) 30 min (c) 60 min. Images were scanned with bias voltage 1 V, and tunnelling current 0.3 nA.
Figure 5.12  Surface area increase as a function of oxygen exposure time after exposure Pd(110) to (a) 10 Torr O$_2$ at 600 K for 1-60 min and (b) 150 Torr O$_2$ at 600 K for 1-60 min.
Chapter

6 Oxygen Dissolution in Pd(111)
Abstract

The near surface and bulk diffusion of oxygen in Pd(111) after an exposure to 1 Torr O$_2$ for 10 min at temperatures 600-900 K was studied by Temperature Programmed Desorption (TPD), Auger-electron Spectroscopy (AES), Low Energy Electron Diffraction (LEED) and Scanning Tunneling Microscopy (STM). During the exposure, a two dimensional surface oxide was formed which disappeared when the sample was quenched in vacuum. Under the exposure conditions, oxygen dissolved into Pd near surface region without the formation of bulk PdO. The desorption of near surface oxygen occurred at 770-870 K. The bulk diffusion of oxygen could be populated by high O$_2$ exposure at elevated temperatures, for instance in 1 Torr O$_2$ at above 820 K, but depleted by Ar$^+$ sputtering and/or flashing in vacuum to 1300 K. The desorption of bulk oxygen peaked at above 1070 K. The oxygen migration into the Pd bulk region helped to increase the oxygen uptake due to the saturation of bulk oxygen reservoir. The $^{18}$O experiment suggested that bulk oxygen did not transform to the near surface oxygen species. The oxygen uptake during 1 Torr O$_2$ exposure in the temperature window from 820 K to 900 K depended on whether the Pd(111) was pre-exposed to O$_2$ during the heating ramp. This was referred as an oxygen uptake hysteresis and was attributed to the formation of surface oxide and near surface oxygen during pre-exposure, which stabilized the surface chemisorbed oxygen on Pd surface.
6.1 Introduction

Palladium is one of the best catalysts for oxidation reactions such as the complete oxidation of hydrocarbons in automotive exhausts and the catalytic methane combustion for energy generation in advanced low-NO\textsubscript{x} emission gas-powered turbines. As compared to other metals, palladium shows the highest rate per unit of metal surface area for methane oxidation [1]. During the combustion reaction, palladium catalyst can exist as either Pd metal or PdO depending on the oxygen partial pressure and the temperature. For instance, in air at atmospheric pressure, the thermodynamically stable phase is PdO at temperatures below 1052 K, while metallic Pd is stable above 1052 K [2-4]. Therefore, in the practical operation of a catalytic combustor, due to the temperature increase with the stages, the oxidation of palladium and the transition from PdO to Pd metallic state at high temperatures may occur.

Since PdO is believed to be more active than Pd metal for methane combustion [5, 6], the reaction rate decreases with an increase of the reaction temperature up to where PdO decomposes; but is found to recover only at a lower temperature than PdO should thermodynamically be formed during catalyst sample cooling. This unusual behavior is referred as a persistent activity hysteresis [7-12].

The dependence of reaction rates on whether the sample is undergoing heating or cooling in a reaction atmosphere is also detected during PdO decomposition and reformation in air [8, 11] or O\textsubscript{2}/Ar mixture [10] using thermogravimetric analysis [8, 11] and gas composition analysis [10]. The decomposition temperature of the PdO measured during heating exceeds the oxide reformation temperature measured during cooling by a few
hundred degrees K [10, 11]. The hysteresis gap between PdO decomposition and reformation is compatible to observed during methane combustion, which indicates that the activity hysteresis is caused by PdO↔Pd transformation hysteresis [8-11].

To elucidate the oxide-metal phase transition hysteresis, some hypotheses have been raised. McCarty [9] and Datye et al. [11] suggested the formation of a strongly chemisorbed layer of oxygen on palladium metal surface during sample cooling, which passivated the surface and inhibited the bulk oxidation. Salomonsson et al. [10] proposed the existence of a non-stoichiometric Pd/O species: PdO\textsubscript{x}. The gas phase O\textsubscript{2} and the two solid phases, Pd and PdO\textsubscript{x} form a three-phase diagram. According to the diagram, palladium decomposition and reformation underwent different paths, thus resulting in the hysteresis. A more complex four-phase diagram was proposed by Wolf et al. [12] which included Pd metal, PdO bulk, surface PdO and chemisorbed oxygen.

The extent of the phase transition hysteresis depends on the supports [8, 13, 14] as well as the oxygen partial pressure [10, 15]. For example, ZrO\textsubscript{2} support and Al\textsubscript{2}O\textsubscript{3} support present large hysteresis effects with the temperature difference for PdO decomposition and reformation of above 200 K in air at atmospheric pressure; in contrast, the hysteresis gap obtained on TiO\textsubscript{2} or CeO\textsubscript{2} support is less than 100 K [8]. Thus, a generic question rises: whether the hysteresis is an intrinsic feature of palladium or entirely due to metal-support interaction? The hysteresis temperature window could be narrowed or eliminated in a higher O\textsubscript{2} pressure [10, 15].

The interaction of palladium with oxygen typically in the high vacuum range (< 10\textsuperscript{-6} Torr, 1 Torr = 133.3 Pa) has been studied extensively, for instance [16-25] and references therein. On Pd(111) surface, adsorption of O\textsubscript{2} at room temperature (RT) results in a (2×2)
\( O_{\text{ads}} \) structure with coverage of 0.25 monolayer (ML, 1 ML = 1.53 \times 10^{15} \text{ atoms cm}^{-2}) [17, 23]. An incommensurate two dimensional surface oxide is formed by exposure of the (111) surface to NO\(_2\) at 500 K [23] or to O\(_2\) [20, 21]. The coverage assigned to the 2D surface oxide ranges from 0.67 ML [20] and 1 ML [21] to 1.0-1.8 ML [23]. Decomposition of the surface oxide results in the formation of hexagonal 1 ML deep holes, which is attributed to the palladium density difference in the surface oxide state and the metallic state [18, 20]. The growth of islands and peninsulas in the vicinity of monoatomic steps on a Pd(111) surface is reported after NO\(_2\) dosing [23]. These islands and peninsulas, formed by palladium atoms expelled from the lattice by interstitial oxygen atoms incorporating with surface oxygen, are assigned as intermediate state between metallic Pd and bulk PdO [23].

The diffusion of oxygen into palladium subsurface and/or bulk region is evidenced at high temperatures [16, 17, 19, 22, 25]. The subsurface oxygen desorbs at above 1100 K [17, 19]. The oxygen species diffused in a polycrystalline palladium foil was suggested to form a Pd-O solid solution: PdO\(_x\) [16].

There is a gap between the surface science studies, which are performed in ideal ultra-high vacuum (UHV) conditions, and the researches carried out on real supported catalysts at atmospheric pressure. To bridge fundamental and applied research, we used a Pd(111) single crystal as a planar model catalyst and analyzed the changes in the surface states using surface science techniques after an exposure to 1 Torr O\(_2\) a relatively high pressure, over a wide temperature range from 600 K to 900 K. The questions regard the oxygen diffusion into Pd near surface and bulk regions, the oxygen uptake dependence on the
sample history and the oxygen uptake hysteresis in the temperature window of 820-900 K in 1 Torr O\textsubscript{2} were addressed in this study.

### 6.2 Experimental methods

The experiments were carried out in a specially designed system, which consisted of three chambers: the UHV analysis chamber, the UHV Scanning Tunneling Microscopy (STM) chamber and the high-pressure reaction cell. The analysis chamber housed facilities for Auger-Electron Spectroscopy (AES), Low Energy Electron Diffraction (LEED), and Temperature Programmed Desorption (TPD). The STM chamber accommodated an ambient-temperature UHV STM (RHK, Inc.). The base pressure in UHV chambers after bake out was $5 \times 10^{-10}$ Torr and in the high-pressure reaction cell was $2 \times 10^{-8}$ Torr. The sample could be transferred between the chambers, without exposure to the atmosphere.

The sample was a 0.8 mm thick, 7.2 mm diameter single crystal Pd(111) (Princeton Scientific) with misorientation $< 0.5^\circ$. The single crystal was mounted on a standard RHK variable-temperature sample holder. The temperature was measured by a chromel-alumel thermocouple spot-welded onto the side of the sample. In the analysis chamber, the sample was heated by electron-bombardment from the rear and the temperature was controlled by a Eurotherm 2408 controller interfaced with a power supply. In the reaction chamber, the sample was heated by an IR lamp also controlled by a Eurotherm 2408 controller. Scanning tunneling microscopy images were obtained using Pt-Ir tips electrochemically etched in NaCl/NaNO\textsubscript{3} melt.
The TPD spectra were collected by means of a RGA-200 mass-spectrometer (Stanford Research System) at a constant heating rate of 5 K s\(^{-1}\). The coverage was calculated by integrating area under a TPD peak and measured in monolayers. Since relatively high uptakes were measured, the maximum coverage of 2.4 ML obtained by exposure to 50 L NO\(_2\) at 500 K was used for calibration [23].

The sample cleaning procedures consisted of repeating cycles of Ar\(^+\) sputtering at room and elevated temperatures, annealing up to 1100 K in UHV, exposure to O\(_2\) and NO\(_2\) followed by flashing at 1100 K for 60 seconds in UHV. The sample cleanliness was checked by TPD, AES and LEED. NO\(_2\) and O\(_2\) were introduced into the analysis chamber through a capillary doser.

Oxygen treatments in 1 Torr O\(_2\) were performed in the high-pressure reaction cell. The following treatment protocol was used unless specially noted. The single crystal was heated up to the desired temperature in vacuum and oxygen was then introduced. After O\(_2\) exposure, the sample was cooled down and oxygen was pumped out simultaneously. It took less than 1 min to cool the sample to 450 K and to reach the vacuum in the reaction chamber better than 10\(^{-6}\) Torr. After a treatment, the sample was transferred into the STM and/or analysis chamber.

### 6.3 Results

#### 6.3.1 Temperature programmed desorption

Figure 6.1 shows a set of oxygen TPD spectra obtained after exposing the Pd(111) single crystal to 1 Torr O\(_2\) for 10 min at temperatures varying from 600 K to 850 K. The single crystal was heated up to 1100 K during TPD. The temperature programmed desorption
spectrum obtained after exposure of the Pd(111) to 12 L NO₂ at 510 K is also shown in the bottom of Figure 6.1 for comparison. The NO₂ dosing resulted in a narrow and symmetric oxygen desorption peak at 750 K with the oxygen coverage equivalent to 1.8 ML. The TPD characteristics observed after 1 Torr O₂ treatment were different. After the oxygen exposure, O₂ desorbed in a single TPD peak with the desorption-maximum shifting from 770 K to 870 K as the exposure temperature increased from 600 K to 850 K. The oxygen uptake on Pd(111) is a strong function of the exposure temperature as shown in Figure 6.2. The oxygen uptake was 7 ML after 600 K treatment, which sharply increased with the exposure temperature and reached the maximum of 113 ML after 820 K treatment. The further increase of the exposure temperature up to 850 K and 900 K resulted in the abrupt decrease in the oxygen uptake to 10 ML and 0 ML, respectively. This was in the temperature range of the thermodynamic transition PdO→Pd, which occurs at 1 Torr O₂ at 895 K [2-4].

The interesting fact is that AES detected the oxygen trace after the 12 L NO₂ dosing, the O/Pd ratio was approximately 0.07; in contrast, no AES oxygen peak was observed on the Pd(111) surface after all the 1 Torr oxygen exposures. LEED revealed a slightly diffused Pd(111) (1×1) pattern. Moreover, measurements of tunneling current versus bias voltage by STM (also referred to as I-V spectroscopy) did not reveal an energy gap expected for the oxide. A band gap of 4.0-5.0 eV is a characteristic of the formation of stoichiometric PdO [26]. Therefore, likely no palladium oxide was formed and the surface remained in a metallic state although the oxide phase is thermodynamically favorable under the O₂ exposure conditions. One might then conclude that either PdO formed during oxygen treatment decomposes while sample is quenched in vacuum; or
stoichiometric PdO is never formed. Oxygen atoms diffused into Pd near surface region. According to Campbell et al. [16], the oxygen species dissolved in palladium might form a solid solution, which was referred as PdO_x. The similar behavior for the dissolution of carbon into Pd to form PdC_x was suggested in References [27-29].

The metallic state of the surface after 1 Torr oxygen exposures was verified by the following experiment, in which NO_2 was adsorbed over the Pd(111) surface pre-treated in 1 Torr O_2 for 10 min at 700 K as shown in Figure 6.3. As suggested by Zheng and Altman [23], PdO inhibits the NO_2 dissociative adsorption and thus the oxygen uptake rolled off once PdO was formed. Therefore, NO_2 is used as a “chemical” probe to detect the chemical state of the surface after oxygen exposure.

As shown in Figure 6.3(a), exposure of a clean Pd(111) surface to 12 L NO_2 at 510 K resulted in a single TPD peak at 750 K with the integral peak area corresponding to an 1.8 ML oxygen coverage. The peak position and its shape were in good agreement with the literature data [23, 30]. The complex LEED pattern observed on the NO_2 adsorbed Pd(111) surface was identical to that of a two dimensional surface oxide [21, 23].

Exposure of a clean Pd(111) surface to 1 Torr O_2 at 700 K for 10 min, O_2 desorbed in a single slightly asymmetric peak with the desorption-maximum at 840 K (Figure 6.3(b)). Figure 6.3(c) shows the O_2 desorption spectrum obtained by exposing a Pd(111) surface pre-treated in 1 Torr O_2 at 700 K for 10 min to 12 L NO_2 at 510 K. The TPD trace revealed two O_2 desorption peaks at 750 K and 840 K, respectively. The peak at 840 K characterized the desorption of oxygen dissolved in the near surface region during 1 Torr exposure at 700 K (Figure 6.3(b)), whereas the peak at 750 K is a feature of NO_2 adsorption (Figure 6.3(a)). The intensity of the latter was depressed by approximately
two times in comparison with the corresponded value for NO$_2$ adsorption on a clean Pd(111) surface. The complex LEED pattern of the 2D surface oxide was again observable on the Pd(111) surface after this treatment. This experiment demonstrated that the palladium surface after 1 Torr oxygen treatment was indeed in a metallic state.

The change of the treatment protocol described in Experimental Section revealed the other phenomenon. Usually the sample was cooled down and oxygen was pumped out simultaneously. LEED showed a diffused ($1 \times 1$) diffraction pattern after oxygen treatment in the temperature range from 600 K to 820 K. The complex LEED pattern, which characterized the 2D surface oxide [21, 23], was however observed after an exposure to 1 Torr O$_2$ for 10 min at 600-820 K followed by cooling the sample in oxygen pressure to 400 K in approximately 2 min before transferring to analysis chamber. It has been suggested that this oxide structure could be “frozen in” by reducing the sample temperature in O$_2$ pressure [21]. This observation is an indication that 2D surface oxide was indeed formed as an intermediate state between metallic Pd and bulk PdO during the 1 Torr O$_2$ treatment, which then transformed into the dissolved species and/or desorbed as O$_2$ when the sample was quenched in vacuum.

6.3.2 Scanning tunneling microscopy

Morphology of the Pd(111) surface after 1 Torr O$_2$ treatments for 10 min at 600 K and 700 K was monitored by STM as shown in Figure 6.4 and Figure 6.5. Small clusters with mean size of 6 Å appeared on the surface after 1 Torr O$_2$ at 600 K (Figure 6.4(a) and (b)). The mean distance between the clusters was 5 Å and the z corrugation was 1.3 Å. The step height increased up to 2.45 ± 0.1 Å, compared to the step height of the clean Pd(111)
surface of 2.25 ± 0.05 Å. A number of holes with the mean size of 3 nm and the depth of 2.4 ± 0.1 Å appeared. The holes covered about 30% of the Pd(111) surface. This surface morphology was quite similar to those reported after decomposition of the 2D surface oxide [18, 20]. Hexagonal 1 ML deep holes were observed after a 2D surface oxide on Pd(111) reduced in 25 L CO at 573 K [18]. Besides the holes, there were a few islands up to 3 nm in size, expelled from the terraces. The island height was same as the one for the steps and the holes and equal to 2.45 ± 0.1 Å, independent on the sample bias. The terraces, which were approximately 300-400 Å in width, narrowed up to 100-150 Å after oxygen treatment.

The number of the holes increases, but the size of the holes decreases after exposure of the Pd(111) crystal to 1 Torr O₂ at 700 K for 10 min as shown in Figure 6.5. The coverage of the holes remained approximately 30% on the surface. Some of the holes lost their original hexagonal or square shape and elongated in the directions parallel to the steps. The depth of the holes and the step height remained unchanged as after 1 Torr treatment, but the step edges became more curved, no longer straight as on the clean Pd(111) surface.

### 6.3.3 Oxygen uptake dependence on sample history

It is found that the oxygen uptake on Pd(111) depends on the sample history as shown in Figure 6.6. The freshly-cleaned (Ar⁺ sputtering followed by annealing to 1100 K) single crystal showed the uptake of 26 ML after 1 Torr O₂ treatment at 700 K for 10 min. The uptake was determined by TPD with heating up to 1000 K. Repeating the 1 Torr O₂ exposure at 700 K resulted in the gradual increase of the oxygen uptake from 32 ML after
the second treatment, to 33 ML after the third treatment and to 34 ML after the fourth treatment. The uptake reached 38 ML when the Pd(111) single crystal was pre-exposed to 1 Torr O2 at 900 K for 10 min and then flashed to 1000 K. Before the sixth treatment, sample was cleaned by Ar\textsuperscript{+} sputtering followed by annealing to 1100 K in UHV. The uptake amount dropped drastically to the initial level of 26 ML. The maximum uptake of 38 ML was however recovered by the pre-treatment in 1 Torr O2 at 900 K without undergoing treatments at 700 K; and this amount of 38 ML was steady, not increasing with further 700 K treatment. Pre-annealing the Pd(111) single crystal at 1300 K in UHV caused the uptake to decrease down to 26 ML.

We have shown in Figure 6.1 and Figure 6.3 that the O2 desorption after the 700 K oxygen exposure is complete at around 950 K. As the TPD was performed up to 1000 K in the experiments, the possibility for the desorption of incompletely desorbed O2 from previous treatments could be excluded as a cause for the uptake amount increase with repeating the 700 K treatments (Treatment cycle 1 to 4). Moreover, no oxygen TPD trace below 1000 K was found after O2 treatment at 900 K. Thus, the oxygen species formed during the high-temperature treatment should not contribute to the oxygen uptake (Treatment cycle 6 and 8). Therefore, we have to invoke another mechanism to elucidate the dependence of the oxygen uptake on the sample history. As a possibility, oxygen diffuses into Pd bulk region and builds up a so-called “bulk oxygen reservoir”. The bulk oxygen was suggested to be populated by high O2 exposure at elevated sample temperatures [17, 22], while be depleted by Ar\textsuperscript{+} sputtering and/or sample annealing at much higher temperatures for example 1142 K [19]. The oxygen bulk diffusion might change the adsorption potential of the surface and therefore affect the oxygen near
surface diffusion [31, 32]. Note that, to differentiate from the near surface oxygen, we referred to this oxygen species as bulk oxygen, not subsurface oxygen as referred in some of the literature [17, 22].

6.3.4 Bulk oxygen

The dissolution of oxygen into Pd bulk region became distinguishable on Pd(111) after exposure to 1 Torr O₂ at above 820 K for 10 min. The TPD spectra obtained up to 1300 K are displayed in Figure 6.7. Prior to each O₂ treatment, the sample was cleaned by Ar⁺ sputtering followed by annealing to 1100 K. It is shown by the Trace-a in Figure 6.7 that besides the peak located at 870 K, a high-temperature desorption peak at 1130 K appeared after 1 Torr O₂ exposure at 820 K. Here, the peak at 870 K characterized the desorption of the oxygen species dissolved in Pd near surface region during 1 Torr exposure at 820 K (see also Figure 6.1); and the peak at 1130 K was assigned to the desorption of bulk oxygen. The intensity for the high-temperature TPD peak enhanced with an increase in the treatment temperature, and corresponded to 2 ML after 820 K treatment and 8 ML after 900 K treatment. As shown by the Trace-c, the high-temperature TPD peak shifted towards a lower temperature of 1070 K after the O₂ exposure at 900 K. The fact that no TPD feature was revealed on a sample treated by Ar⁺ sputtering followed by annealing to 1100 K right after the 1 Torr O₂ exposure at 900 K was an indication that the oxygen species in the bulk region was depleted by Ar⁺ sputtering.

How would the oxygen uptake on Pd(111) increase with the population of the bulk oxygen achieved by high temperature O₂ exposure? One possibility is a portion of the
oxygen in the bulk region converts to the near surface oxygen and desorbs at lower temperatures characteristic of the near surface dissolved oxygen species. To test this hypothesis, labeled O₂ (¹⁸O₂) was used as a reactant to differentiate from ¹⁶O₂. The Pd(111) single crystal pre-flashed to 1300 K in UHV, was exposed to 1 Torr ¹⁸O₂ at 900 K for 10 min, and then the sample was quenched in vacuum to 400 K followed by another exposure to 1 Torr ¹⁶O₂ at 700 K for 10 min. The TPD spectra for ¹⁸O₂ and ¹⁶O₂ obtained up to 1300 K are represented in Figure 6.8. The ¹⁸O₂ desorption trace (Trace-a) showed three peak maxima occurred at 840 K, 1070 K and 1130 K, respectively. The intensity for the desorption at 840 K corresponded to an oxygen uptake of only 0.2 ML; while the high-temperature TPD peaks were equivalent to a total uptake amount of 4 ML. The ¹⁶O₂ desorption trace (Trace-b), similar to that in Figure 6.1 and Figure 6.3, peaked at 840 K with the integral peak area equivalent to 26 ML. This result was an indication that the oxygen species in the bulk region is stable, which does not transform to the near surface oxygen species under the treatment conditions. The 0.2 ML ¹⁸O₂ desorption at 840 K (Trace-a) most likely came from the ¹⁸O₂ isotope originally presented in the reactant of ¹⁶O₂.

6.3.5 Hysteresis

The oxygen uptake on Pd(111) after exposure to 1 Torr O₂ for 10 min in the temperature window of 820-900 K was found to depend on whether the single crystal sample was pre-exposed to O₂ during the heating ramp from RT to the exposure temperature. A typical example was illustrated in Figure 6.9, in which the TPD spectra were obtained after 1 Torr O₂ exposure at 850 K performed according to three different protocols. Trace-a, also seen in Figure 6.1, was obtained after 10 min exposure at the standard oxygen
treatment conditions as described in Experimental Section. A small O₂ desorption peak was observed at 870 K. The sample surface was still in metallic state as monitored by AES and LEED. Pre-heating the sample in 1 Torr O₂ from RT to 850 K at a heating rate of 2.5 K s⁻¹ followed by the 10 min oxygen exposure produced a strong, broad and asymmetric peak centered at 895 K as shown in Trace-c. The Auger peaks of oxygen located at 490 and 510 eV were observable, in addition to the Pd Auger features. The O/Pd atomic ratio was approximately 0.12. LEED revealed a very weak and diffuse (1×1) pattern. These results suggested the formation of bulk PdO. Flashing the single crystal sample to 850 K in 1 Torr O₂ at 2.5 K s⁻¹ followed by quenching in vacuum (without holding at 850 K) gave the Trace-b. The O₂ desorption maximum in Trace-b occurred at 850 K. The oxygen uptakes after the three treatments were 10 ML (Trace-a), 29 ML (Trace-b) and 163 ML (Trace-c), respectively; and the irreversibility in the oxygen uptake was manifested by the uptake amount difference between obtained on Trace-c (163 ML) and the summation on Trace-a and Trace-b (39 ML). This irreversibility is referred as oxygen uptake hysteresis.

The temperature window for the uptake hysteresis on Pd(111) in 1 Torr O₂ was revealed in Figure 6.10, in which Curve-a represented the oxygen uptake on a sample pre-heated in vacuum and then exposed to oxygen for 10 min (the condition to provide the TPD spectrum in Figure 6.9, Trace-a). Curve-c summarized the uptake amount on the sample pre-heated in 1 Torr O₂ to the exposure temperature at 2.5 K s⁻¹ and held for 10 min (the condition to produce the TPD spectrum in Figure 6.9, Trace-c). Subtraction of the uptake obtained on the flashed-in-oxygen sample (the condition to give the TPD spectrum in Figure 6.9, Trace-b) from that on curve-c was illustrated on curve-b.
6.4 Discussion

6.4.1 Oxygen species formed on Pd(111) after O$_2$ exposure

We found completely five types of oxygen species formed on Pd(111) during O$_2$ exposure depending on the Pd-O interaction. Dissociative adsorption of O$_2$ at RT results in a p(2×2) overlayer with 0.25 ML saturated coverage [17, 23]. The two dimensional surface oxide, characterized by the complex LEED pattern [21, 23] distinct from that of PdO or the original metallic facet, is formed by exposure of the (111) surface to 12 L NO$_2$ at 510 K. The coverage is 1.8 ML under this condition.

The near surface and bulk diffusion of oxygen becomes energetically feasible when the oxygen uptake increases beyond the surface saturation coverage as a consequence of the reduced oxygen binding energy. The near surface diffusion of oxygen, without the formation of bulk PdO, was observed after an exposure of Pd(111) to 1 Torr O$_2$ at above 600 K (Figure 6.1). A similar observation on a Pd polycrystalline foil was reported by Campbell et al. [16]. After exposing the Pd foil at 1023 K in 10$^{-2}$ Torr O$_2$, an equivalent of 350 ML oxygen was detected to incorporate into the Pd metal without the formation of PdO [16]. This oxygen species was suggested to form the solid solution of PdO$_x$ [16]. To accommodate the interstitial oxygen atoms, the Pd crystal structure was expanded and manifested by an outward expansion of the inter-planar spacing for the first two surface layers. The monatomic step height increased by 0.2 Å from the original 2.25 Å on Pd(111) after an exposure to 1 Torr O$_2$ at 600 K and 700 K for 10 min. This oxygen near surface diffusion involves a temperature-activated step (Figure 6.2). The activation
energy was determined to be 82 kJ mol\(^{-1}\) in the temperature range between 600-780 K [33].

The bulk diffusion of oxygen occurs at a temperature above 523 K was suggested by Leisenberger et al. [19], and became populated by 1 Torr O\(_2\) exposure at above 820 K (Figure 6.7). The bulk oxygen is tightly bounded so that it only desorbs from the surface at 1142 K [19] or above 1070 K (Figure 6.7 and Figure 6.8), comparing to the desorption of chemisorbed oxygen peaked at 750-850 K [17, 19, 23] or the decomposition of surface oxide at 725-750 K (Figure 6.3) [17, 19, 23, 30]. The amount of the oxygen species in the bulk region increased with an increase in the O\(_2\) treatment temperatures as shown in Figure 6.7, which suggests that the bulk diffusion is also a temperature-activated process as the near surface diffusion.

There are, however two noticeable differences between the near surface oxygen and the bulk oxygen. The desorption of near surface oxygen occurs at much lower temperatures as compared with that of the bulk oxygen. The TPD spectra peaked at 770-870 K after treatments in 1 Torr O\(_2\) at 600-850 K for 10 min (Figure 6.1), similar to that for the surface chemisorbed oxygen and the surface oxide. This fact suggests that the oxygen species in the near surface region is in equilibrium with the adsorbed oxygen, the desorption of near surface oxygen could be rate-determined by the desorption of surface oxygen. Another difference is revealed that the near surface oxygen dissolution terminates in the same temperature range as the thermodynamic transition of PdO↔Pd (895 K in 1 Torr O\(_2\)) [2-4]; whereas more oxygen atoms are found to diffuse into the bulk region at 900 K. We did not find evidence that the bulk oxygen could transform to the
chemisorbed oxygen or surface oxide or the near surface dissolved oxygen species (Figure 6.8).

The near surface oxygen is likely a precursor to the formation of bulk PdO. The concentration of near surface oxygen increases as the oxygen atoms diffuse into Pd metal continuously [33]. At a certain critical concentration, a new phase nucleates and grows. The formation of bulk PdO is observed after the treatments at 600 K in O₂ above 50 Torr for 10 min or in 10 Torr O₂ but for prolonged exposure time above 60 min [33].

To summarize the five oxygen species, we propose the mechanism for palladium oxidation. Consistent with previous studies [17, 22], the mechanism consists of the following stages:

\[
\begin{align*}
\text{O}_2(\text{gas}) & \leftrightarrow \text{O(adsorption)} & (1) \\
\text{O(adsorption)} & \leftrightarrow \text{O(surface oxide)} & (2) \\
\text{O(adsorption)} & \leftrightarrow \text{O(near surface)} & (3) \\
\text{O(adsorption)} & \rightarrow \text{O(bulk)} & (4) \\
\text{O(near surface)} & \rightarrow \text{O(bulk oxide).} & (5)
\end{align*}
\]

There are equilibriums between (1) O₂ in the gas phase O₂(gas) and the chemisorbed oxygen atoms O(adsorption); (2) O(adsorption) and the 2D surface oxide O(surface oxide); (3) O(adsorption) and the oxygen species dissolved in the near surface region O(near surface). But the transformation of (1) O(adsorption) to the oxygen species in the bulk region (bulk); and (2) the oxidation process from O(near surface) to O(bulk oxide) are irreversible.
6.4.2 Bulk oxygen

The amount of oxygen uptake on Pd(111) increased with the population of the bulk oxygen; while decreased by depleting this oxygen species (Figure 6.6). The dependence of the oxygen uptake on the sample history is similar to that observed previously by Conrad et al. [17] who found that the oxygen desorption from the chemisorbed state enhanced in the intensity with increasing the amount of bulk oxygen. It was also shown by Meusel et al. [31, 34] that less oxygen was initially available to the surface reaction for CO oxidation on supported Pd nano particles; only after the bulk oxygen reservoir was built up, stable reaction rate could be detected. Then how would the bulk oxygen affect the uptake process? We have excluded the possibility for the conversion from bulk oxygen to the near surface oxygen. Therefore, other mechanism has to be invoked.

It has been shown that the oxygen uptake on Pd(111) exposed to high-pressure O$_2$ (1-150 Torr) at elevated temperatures (600-820 K) is indeed oxygen near surface diffusion limited [33]. Since the oxygen diffusion into the near surface region is competing with the diffusion into bulk region for surface adsorbed oxygen (Pd oxidation mechanism reaction sequences 3 and 4), only when the bulk oxygen reservoir is saturated, in other words, the reaction sequence 4 is terminated, the highest near surface oxygen diffusion rates could be obtained.

6.4.3 Hysteresis

The irreversibility in the oxygen uptake during 1 Torr O$_2$ exposure at high temperatures from 820 K to 900 K has been shown in Figure 6.9 and 6.10. Oxygen dissolved readily in Pd(111) near surface region when the sample was pre-exposed to O$_2$ during the heating
ramp; whereas, the oxygen near surface dissolution was terminated abruptly at around 830 K when the sample was heated up to the exposure temperature in vacuum. This oxygen uptake hysteresis occurs in the same temperature window as of the PdO ↔ Pd transformation hysteresis [8-11], which has previously been attributed to the formation of a passive chemisorbed oxygen layer on the metal surface at high temperatures. This passive chemisorbed oxygen was suggested to prevent the diffusion of oxygen and subsequently the formation of bulk PdO [9, 11]. However, it is well established that chemisorbed oxygen is the precursor for the near surface and bulk dissolved oxygen [17, 22]. Another argument to this attribution comes from the question: If there existed this passive adsorbed oxygen layer, why it does not prevent oxygen dissolution at a lower temperature out of the hysteresis range?

We have proposed the mechanism for palladium oxidation, in which we suggest that there exists an equilibrium between O₂(gas) and O(adsorption) (reaction sequence 1). The heat of adsorption of oxygen on the Pd(111) surface at a coverage around 0.25 ML is roughly –220 - –230 kJ mol⁻¹ [17, 35]. Therefore, increase the O₂ exposure temperature would shift the equilibrium to the left side of desorption. The prevailing process of oxygen desorption at high temperature would result in a low concentration of adsorbed oxygen on the Pd(111) surface. In addition, the reaction sequences 2 through 4 suggest the competitions among the transformations from O(adsorption) to (1) O(surface oxide), (2) O(near surface) and (3) O(bulk). The irreversible diffusion of oxygen into Pd bulk region was accelerated at above 820 K (Figure 6.7), which led to a rapid depletion of the surface oxygen reservoir [31], and thus masks the oxygen near surface dissolution. Since O(near surface) is the precursor to the O(oxide) (reaction sequence 5), which is formed
only when a critical concentration of O(near surface) is reached, there is no formation of the bulk PdO at the high temperature when the O2 desorption is prevailing over adsorption.

In a different scheme that the sample was pre-heated in O2 to reach the exposure temperature above 820 K, a 2D stable surface oxide was formed during the heating ramp, and oxygen atoms diffused into the near surface region (reaction sequences 2 and 3). It is well established that the kinetics is autocatalytic for the reversible series reactions: O(surface oxide) \leftrightarrow O(adsorption) \leftrightarrow O2(gas) (reaction sequences 1 and 2), because the concentration of O(adsorption) needs to be increased at first in order to increase the O2 desorption rate [18]. The same assumption of the autocatalytic reaction kinetics can be made for the reversible series reactions: O(near surface) \leftrightarrow O(adsorption) \leftrightarrow O2(gas) (reaction sequences 1 and 3). Presumably that the Pd(111) surface was saturated with 2D surface oxide by the O2 exposure during the heating ramp, the O(adsorption) will become available from O(surface oxide) and/or O(near surface) at a higher temperature, so as to the oxygen desorption [18, 36]. The increased desorption temperature thus reserved a reasonable surface oxygen concentration and the high oxygen uptake rates until the PdO decomposition temperature.

It should be noted that since the oxygen uptake hysteresis was found on a non-support Pd single crystal, the hysteresis is then an intrinsic behavior of Pd metal.

6.5 Summary

Oxygen interaction with a Pd(111) single crystal was studied by STM, LEED, TPD, and AES in 1 Torr O2 at a wide temperature range from 600 to 900 K. Oxygen dissociatively
adsorbed on the palladium surface and then diffused into Pd near surface and bulk regions without the formation of bulk PdO. The near surface diffusion of oxygen competed with the bulk diffusion process. The transformation of the adsorbed oxygen atoms into a two dimensional surface oxide was also observed.

The near surface dissolution of oxygen was temperature activated. The maximum uptake amount of 113 ML was determined after an exposure to 1 Torr O₂ at 820 K for 10 min. The oxygen dissolution in Pd resulted in the expansion of lattice structure. After 1 Torr oxygen treatment at 600 K, the step height was measured to be 2.45 ± 0.1 Å, which was almost 9% higher than the steps on the clean Pd(111) surface.

The oxygen uptake on Pd(111) increased with the population of bulk oxygen which was achieved by high O₂ exposure at elevated temperatures, for example in 1 Torr O₂ above 820 K. Saturation of the bulk oxygen reservoir ensured a higher rate for oxygen near surface dissolution rate. Ar⁺ sputtering and/or flashing to 1300 K depleted the bulk oxygen species.

The oxygen uptake hysteresis was found in a temperature window of 820-900 K during exposure of a Pd(111) surface to 1 Torr O₂. This suggested that the hysteresis is an intrinsic feature of palladium. Because of the high rates for O₂ desorption oxygen bulk diffusion at high temperatures above 820 K, atomic oxygen did not diffuse into the near surface region on a sample presented a surface in metallic state. However, 2D surface oxide and near surface oxygen were formed when the Pd(111) sample was pre-exposed to O₂ during the heating ramp. The autocatalytic kinetics for the phase transformation from surface oxide and/or near surface oxygen to surface adsorbed oxygen shifted the oxygen
desorption to higher temperature, and therefore reserved a reasonable adsorbed oxygen surface concentration and the high uptake rates.
REFERENCES


Figure 6.1  
TPD spectra of O$_2$ obtained after exposure of the Pd(111) single crystal to 1 Torr O$_2$ for 10 min. Exposure temperatures are written from the left. TPD was performed up to 1100 K. The TPD spectrum obtained by 12 L NO$_2$ dosing at 510 K was shown in the bottom.
**Figure 6.2** Oxygen uptakes on Pd(111) as a function of treatment temperature after exposure to 1 Torr O$_2$ for 10 min. The uptake amount was determined by repeating the oxygen exposure until a constant uptake was obtained.
Figure 6.3  Oxygen TPD spectra obtained after exposure of the Pd(111) single crystal to (a) 12 L of NO₂ at 510 K; (b) 1 Torr O₂ at 700 K for 10 min; and (c) 1 Torr O₂ at 700 K for 10 min and then to 12 L of NO₂ at 510 K.
Figure 6.4  STM images of a Pd(111) surface exposed to 1 Torr O$_2$ at 600 K for 10 min. The rectangular area of image (a) is shown at high magnification in (b). The images were collected at bias voltage 0.1 V and tunnelling current 0.1 nA.
Figure 6.5  STM images of a Pd(111) surface exposed to 1 Torr O₂ at 700 K for 10 min. The image was collected at bias voltage 0.1 V and tunnelling current 0.1 nA.
Oxygen uptake on Pd(111) single crystal exposed to 1 Torr O<sub>2</sub> at 700 K for 10 min depending on the sample history. Exposure of the Pd(111) surface to 1 Torr O<sub>2</sub> at 700 K for 10 min is referred to as ‘treatment’. Ar<sup>+<sup> sputtering was followed by annealing in UHV to 1100 K. The sample was flashed up to 1000 K after 900 K exposure in 1 Torr O<sub>2</sub> for 10 min.
Figure 6.7  TPD spectra of $O_2$ obtained after exposing the Pd(111) single crystal to 1 Torr $O_2$ for 10 min at (a) 820 K, (b) 850 K and (c) 900 K. TPD was carried out up to 1300 K.
Figure 6.8  TPD spectra of (a) m/e = 36 and (b) m/e = 32 after exposure the Pd(111) single crystal to 1 Torr of $^{18}$O$_2$ at 900 K for 10 min and then to 1 Torr of $^{16}$O$_2$ at 700 K for 10 min. TPD was carried out up to 1300 K.
Figure 6.9  TPD spectra of O$_2$ obtained on a Pd(111) single crystal (a) exposed to 1 Torr O$_2$ at 850 K for 10 min (the sample was heated first and then O$_2$ was introduced); (b) flashed in 1 Torr of O$_2$ up to 850 K at the heating rate 2.5 K s$^{-1}$; (c) heated to 850 K in 1 Torr O$_2$ at the heating rate 2.5 K s$^{-1}$ and held at 850 K for 10 min.
Figure 6.10  The oxygen uptake on a Pd(111) single crystal obtained after exposure to 1 Torr O₂ at specified temperature: the filled circles are for the sample heated in vacuum and then exposed to O₂ (like TPD spectrum in Figure 6.9, Trace a), the open circles are for the sample heated at 2.5 K s⁻¹ in O₂ to the exposure temperature and held for 10 min (like TPD spectrum in Figure 6.9, Trace c), the half-filled circles are after the subtraction of the uptake obtained for the flashed-in-oxygen sample from the one for the heated-in-oxygen & held sample (like the area under TPD peak of spectrum Trace c minus the corresponding value for spectrum Trace b in Figure 6.9).
Chapter

7 Increase of Pd Surface Area by Treatment in Dioxygen
Abstract

The surface area of Pd(111) and Pd(110) single crystals increased after oxidation in O₂ transformed them to PdO. The surface area of the oxide decreased after complete reduction in H₂. The techniques of STM, TPD, XPS, AES and LEED were employed to study the Pd(111) and Pd(110) single crystal surfaces after they were subjected to O₂ oxidation, methane combustion and H₂ reduction. The surface area of the treated palladium single crystals was measured by ¹⁸O isotope exchange and by direct measurements using the STM image. These two methods showed agreement within 20%. After oxidation in O₂ (100 and 150 Torr) at 600 K, the surface area for both Pd(111) and Pd(110) single crystals increased by a factor of approximately two. The effect was more pronounced on the Pd(111) surface. The oxidized surfaces were covered with 3-4 nm semi-spherical oxide agglomerates that formed a “cauliflower-like” structure 10-20 nm in size. Similar surface structures were observed after exposure of the Pd single crystals to a lean O₂ and CH₄ reaction mixture (O₂:CH₄ = 10:1). Thus, the oxidized single crystal becomes amorphous. Reduction in H₂ decreased the surface area of the pre-oxidized Pd(111) and Pd(110) crystals. An amorphous metallic surface was produced after H₂ reduction at 373 K, whereas a smooth surface with characteristic single crystal features was observed after reduction at 673 K. These experiments suggest that oxidizing a Pd metal catalyst or reducing an oxidized Pd catalyst, for example before palladium metal surface area measurement, will affect the surface area of the sample. It also shows that the increase in surface area on Pd catalysts after oxidation treatment is caused by surface roughening.
7.1 Introduction

The turnover rate (TOR) is defined as the number of molecules reacted on an active site per unit of time [1]. It is one of the most important parameters used in quantifying the properties of a catalyst [2, 3]. To calculate the TOR, it is necessary to know the number of active sites, a rarely known parameter. In practice, the total surface area is measured and the total number of sites is calculated from it by assuming a certain site density. For example, the adsorption of H₂, O₂, CO and H₂-O₂ titration are used to measure the surface area of supported metal catalysts [1, 4], but the catalyst must be in the reduced state for these techniques to work; in many cases the active catalyst is not in metallic form. Palladium, which is referred to as the most active catalysts for methane combustion [5], is an example. Depending on the oxygen partial pressure and the temperature, either Pd metal or Pd oxide can be the thermodynamically stable phase. In air at atmospheric pressure, PdO is the active phase up to 1073 K [6-8]. Therefore, the oxidized samples will have to be reduced to Pd metal (usually in H₂, see for example [9-11]) before the measurement of surface area by chemisorption. It is implicitly assumed then that the surface area does not change after PdO reduction or Pd oxidation. In general, the surface area may change during reduction. Indeed, H₂ reduction has been suggested to modify the surface morphology and the effect varies with the treatment temperature [12, 13]. The possible changes in surface area after reduction and oxidation prompted us to study the effect of reduction and oxidation on surface area. A direct consequence of accurate measurements on PdO surface area is to allow for the proper measurement of turnover rates. The surface morphology of palladium oxide formed on Pd(111) and Pd(110) single
crystals and the influence of H\textsubscript{2} reduction on the oxidized surfaces were studied by scanning tunneling Microscopy (STM) and temperature programmed desorption (TPD). The surface area measurements were carried out by $^{18}$O isotope exchange [14, 15] and by surface area integration of STM images. We will show that after oxidation in O\textsubscript{2} (100 and 150 Torr) at 600 K, the surface area for both Pd(111) and Pd(110) single crystals increases by a factor of approximately two and that reduction in H\textsubscript{2} decreases the surface area. Thus, one should realize when working with Pd catalysts that there will be variation of surface area after oxidation and reduction treatments.

7.2 Experimental Methods

The experiments were carried out in a specially designed system, which consisted of three chambers: ultra-high vacuum (UHV) analysis chamber, UHV STM chamber and high-pressure reactor. The analysis chamber was equipped with X-ray photoelectron spectroscopy (XPS), Auger-electron spectroscopy (AES), low energy electron diffraction (LEED), and TPD. The STM chamber accommodated an ambient-temperature UHV STM (RHK, Inc.). The base pressure in the UHV chambers were $5 \times 10^{-10}$ Torr (1 Torr = 133.3 Pa). The high-temperature/high pressure treatments were carried out in the high-pressure reactor (base pressure $2 \times 10^{-8}$ Torr). The sample could be transferred between the chambers, without exposure to the atmosphere, by means of a 142 cm long transfer arm.

The 0.8 mm thick, 7.2 mm diameter Pd(111) and 1 mm thick, 8.5 mm diameter Pd(110) single crystals (both Princeton Scientific Corp., mis-alignment $< 0.5^\circ$) were used as planar model catalysts. The temperature was measured by a chromel-alumel
thermocouple spot-welded onto the side of the sample. In the analysis chamber, the sample was heated by electron-bombardment from the rear. In the reaction chamber, the sample was heated by an infrared lamp (Research, Inc.) from the front.

The temperature programmed desorption spectra were collected at a constant heating rate of 5 K s⁻¹. The coverage was calculated by integrating the area under the TPD peak and measured in monolayers (1 monolayer = 1 ML = 1.53 × 10¹⁵ atoms cm⁻² on Pd(111) and 0.94 × 10¹⁵ atoms cm⁻² on Pd(110)) by comparing to standard calibration values [16, 17]. STM images were obtained using Pt-Ir tips electrochemically etched in NaCl/NaNO₃ melt. The areas presented here are an average of at least 10 images; the variation in the area among the images is about 20%.

The crystal cleaning procedures consisted of cycles of Ar⁺ sputtering at room and elevated temperatures, flashing in UHV, exposure to O₂ and NO₂ followed by annealing at 1100 K for 60 seconds in UHV. The sample cleanliness was checked by TPD, AES and LEED. The NO₂ and O₂ gases were introduced into the analysis chamber through a capillary dozer.

The following experimental protocol was used for H₂ reduction experiments. The single crystal was oxidized for 30 min in 150 Torr of O₂ at 600 K and then cooled to room temperature (RT) before oxygen was pumped out. The oxidized sample was heated to the desired reduction temperature at a pressure in the reaction chamber better than 10⁻⁷ Torr and then 1 Torr of H₂ was introduced for 1 min. The H₂ was evacuated at a pressure better than 10⁻⁶ Torr before the reduced sample was cooled to RT.
The crystal structure of the oxide formed on the surface of Pd single crystals by oxidation in 150 Torr O₂ at 600 K for 30 min was checked by X-Ray Diffraction (XRD, Rigaku Geigerflex) with CuKα radiation source and a Ni filter. The sample was dismounted from the standard STM sample holder before analysis by XRD.

The combustion of methane on Pd single crystals was performed in the 615 cm³ batch reactor with reaction gases being introduced from a gas manifold in the following order: N₂ (624 Torr), O₂ (160 Torr) and finally CH₄ (16 Torr). The reactants were mixed for 30 min before reaction by a circulation pump model MB-21 (Metal Bellows, Inc.) at a nominal rate of 1000 cm³ min⁻¹. Reaction (600 K) was normally carried out for 60 min with about 2.5% of the CH₄ being consumed. The reaction mixture was analysed with an Agilent 6890 Series gas chromatograph using a thermal conductivity detector, and a 15-ft Carboxen 1000, 60/80 mesh column.

The ¹⁸O isotope exchange experiment was performed in the high pressure reactor following the procedure described before [14]. Briefly an oxidized palladium sample was exposed to 5 Torr ¹⁸O₂ at 600 K for 12 s, and the uptake of ¹⁸O exchanged was then measured by TPD analyzing all gases containing labelled oxygen.

7.3 Results

7.3.1 Surface area measurements: STM image analysis and ¹⁸O isotope exchange

The surface areas were measured by STM image analysis and ¹⁸O isotope exchange. The method using STM images relies on the generation of the surface topographic image by STM and therefore can be used for samples that are conductors and that can be outlined by the microscopy tip. The surface area is then calculated by taking discrete image pixels
and joining three contiguous points to make one triangle. Integration of the area of individual triangle gives the total area. In detail, each STM image is collected as a grid of 512x512 points. Each point (i,j) of a STM image can be described in Cartesian coordinates by xi,j, yi,j, zi,j (x-, y-, z- projections). Three adjacent points, for instance (xi,j yi,j zi,j), (xi+1,j yi+1,j zi+1,j) and (xi,j+1 yi,j+1 zi,j+1) are used to construct a 3D oriented triangle. The total surface area is obtained by summing all triangle areas for each i and j from 1 to 512. Since other triangles can be constructed on other sets of the adjacent points, for instance (xi,j yi,j zi,j), (xi,j+1 yi,j+1 zi,j+1) and (xi+1,j+1 yi+1,j+1 zi+1,j+1), the surface area is averaged through the possible choice of triangles. No filtering or smoothing process was applied to the STM images prior to surface area calculations.

The 18O isotope exchange method is based on the detailed characterization of the 18O exchange kinetics by Au-Yeung et al. [18]. The conditions described in the experimental methods section were designed to ensure that the exchange between 16O in PdO and 18O2 isotope in the gas phase would happen only on the surface, without appreciable 18O diffusion to the bulk. In fact, the rate for recombination of oxygen atoms at the surface of PdO was about 4 s^{-1} at 600 K [18] and this amounts to about 50 turnovers per site in the 12 s the exchange lasts. The number of equivalent-layers that oxygen atoms diffuse under exchange conditions was about 0.05 ML on both Pd(111) and Pd(110) [19]. Thus, only surface oxygen should be exchanged.

The results of the surface area measurement on palladium after oxidation in O2 and catalytic combustion of a lean CH4 mixture (O2:CH4 = 10:1) at 600 K are summarized in Table 7.1. It was found out that the two proposed methods: surface area integration of STM images and 18O exchange agreed within ±20%. In addition, the two methods
provided consistent results with the measurement of the surface area of a polycrystalline Pd foil following CH$_4$ combustion in lean condition [14] which is listed in the last row in Table 7.1.

Table 7.2 provides comparisons on the surface area increase after O$_2$ oxidation of Pd(110), Pd(111), 8.5% Pd/Al$_2$O$_3$ and 10% Pd/ZrO$_2$ [10]. For supported catalysts, the surface areas were determined by H$_2$-O$_2$ titration, after sample reduction. The procedure was described in detail in [10]. Briefly, metallic Pd supported catalysts were prepared by calcination at 1123 K in air for 24 hr followed by quenching to LN$_2$ temperature; metal is the stable phase at these conditions. The oxide phase was then prepared by treating the metallic phase at 973 K in air for 24 hr. Before the surface area measurement by chemisorption, the oxide-supported catalysts were reduced in 1 atm H$_2$ at 373 K for 1 hr. After oxidation, the surface area for the Pd supported catalysts increased approximately by a factor of 2.5 (Table 7.2).

7.3.2 Oxidation of Pd(111) and Pd(110) single crystals

Exposure of the Pd(111) and Pd(110) single crystals to 150 Torr of O$_2$ at 600 K for 30 min resulted in palladium oxide formation, which was monitored by AES and XPS (spectra not shown). The Auger peaks of oxygen were located at 490 and 510 eV, and the O/Pd atomic ratio was approximately 0.7. This value was lower than the expected value for PdO due to electron beam decomposition of the oxide, with the oxygen desorbing as O$_2$ [14, 20]. The core level Pd 3d$_{5/2}$ peak was located at 336.8 eV, shifted 1.8 eV from the metallic peak position at 335.0 eV due to oxidation. On Pd(111) after oxidation, no X-ray diffraction pattern corresponding to PdO could be observed; only the
peaks corresponding to the metal were observable as shown in Figure 7.1. The oxygen uptakes on the Pd(111) and Pd(110) surfaces were 22 ML and 27 ML respectively.

The STM images obtained after exposure of Pd(111) and Pd(110) single crystals to 150 Torr of O\(_2\) at 600 K for 30 min are shown in Figure 7.2. Both oxidized Pd(111) and Pd(110) single crystals showed a similar amorphous PdO surface morphology. The surface was composed of semi-spherical oxide agglomerates that tended to aggregate into a “cauliflower-like” structure. In general, the agglomerate size varied depending on the oxygen pressure and the exposure time. Under the reaction conditions in Figure 7.2, the agglomerates grown on the Pd(111) and Pd(110) surfaces were 4.3 ± 0.7 nm and 3.4 ± 1.1 nm in diameter, respectively. Although the surface roughness did not allow us to draw any conclusion on preferential orientations that the oxide agglomerates grew, prior work has shown that for the Pd(111) surface, the oxide agglomerates appeared first in the vicinity of steps, whereas the \(<1\bar{1}0>\) direction was preferential during the early stages of Pd(110) oxidation [19].

The surface morphologies of Pd(111) and Pd(110) after methane combustion in lean condition at 600 K are presented in Figure 7.3. A clearer “cauliflower-like” structure 20 ± 5 nm in size is visible on both Pd surfaces. The surface area was higher as compared to the oxidized surface in pure O\(_2\), particularly for the Pd(111) surface (Table 7.1).

### 7.3.3 H\(_2\) reduction

To investigate the effect of H\(_2\) reduction on surface morphology, the Pd(111) and Pd(110) surfaces pre-oxidized in 150 Torr of O\(_2\) at 600 K for 30 min were studied after reduction in 1 Torr H\(_2\) at 373 K and 673 K. The lower temperature of 373 K is used for H\(_2–O_2\)
titration on supported Pd catalysts, see for example [9, 10]. The higher temperature of 673 K is used under vacuum for removing adsorbed hydrogen present on Pd after reduction and before hydrogen chemisorption [21]. According to the PdH₉ phase diagram [22], no β-phase palladium hydride is expected under these reduction conditions.

No oxygen was observed by TPD and by AES after the reduction at both 373 K and 673 K, showing that the samples were completely reduced.

The desorption of residual hydrogen was detected by TPD from the Pd(110) surface reduced at 373 K. No LEED pattern was observed after 373 K reduction, which revealed the formation of an amorphous Pd metal overlayer. As shown by STM in Figure 7.4(a) and (c), the surface was rough with metal agglomerates visible. The agglomerates were not of spherical shape as before reduction (see Figure 7.2), but elongated with an aspect ratio around 2-2.5:1 (4.5 ± 0.5 nm vs. 2.1 ± 0.4 nm on Pd(110) and 3.5 ± 0.7 nm vs. 1.6 ± 0.4 nm on Pd(111)). On the Pd(111) surface, the agglomerates were slightly angled with respect to the monatomic steps, which were barely distinguishable. On the Pd(110) surface, the “rod-shaped” agglomerates were aligned along <110>.

Temperature programmed desorption did not reveal any hydrogen desorption after reduction at 673 K. A diffuse (1×1) pattern referred to the bare unreconstructed surface was observed by LEED for both Pd(111) and Pd(110) surfaces. The surface reduced at 673 K were smoother than that after 373 K reduction as shown in Figures 7.3(b) and (d) with monatomic steps visible on the Pd(111) surface. One noticeable difference was that the step was curved and not straight as on a clean Pd(111) surface. Several holes with mean size of 3 nm and mono-atomic depth did not heal on the terraces. A mesoscopic ordered island structure composed of alternating bright and dark islands appeared on the
Pd(110) surface after H₂ reduction at 673 K. The mean size of the island was approximately 14 nm in the <100> direction and 20 nm in the <1\overline{1}0> direction. The height difference between the islands was 0.14 nm, which is equal to the height of the monoatomic step on the Pd(110) surface. Each mesoscopic island was composed of elongated agglomerates with aspect ratio of 3-4:1 (6.9 ± 1.1 nm vs. 2.2 ± 0.6 nm).

The surface area decrease after H₂ reduction is summarized in Table 7.3. It is shown that the surface area of the pre-oxidized Pd(111) and Pd(110) single crystals decreased even after reduction at 373 K, and the effect was more pronounced after 673 K reduction.

7.4 Discussion

7.4.1 STM image analysis and ¹⁸O isotope exchange

We report the surface area integration of STM images and ¹⁸O isotope exchange as methods to measure the surface area on palladium single crystals after O₂ oxidation, CH₄ combustion, and H₂ reduction. In the method of ¹⁸O isotope exchange, the exchange conditions between ¹⁸O in gas phase and ¹⁶O in PdO should be chosen to ensure enough exchange turnovers and to limit bulk diffusion.

In certain circumstances, experimental errors also exist in the STM image analysis method. At low bias voltages STM probes the oxide-substrate interface, whereas STM becomes more sensitive to the vacuum-oxide interface at high bias voltage. This effect was demonstrated for instance by Bertrams et al. [23] for a thin Al₂O₃ film on NiAl(110). No change of the tip height was detected when moving between an Al₂O₃ island and the NiAl substrate at bias voltage below 4 V (the band gap of Al₂O₃ is approximately 7-8 V).
On the other hand, an apparent height of 3.5 Å with respect to the metal support was observed after the bias voltage was increased above 4 V. Hagendorf et al. [24] showed that CoO(001) islands on the Ag(001) surface appeared to be depressed at the bias voltage between −1.5 and +2.2 V, whereas above and below these voltages the islands were protruding from the substrate. The maximum height variation was 6 Å. In our experiments this effect was not significant. The variation of the size and height of the oxide clusters was in the range of 0.1-0.3 Å when the bias voltage was changed from 0.1 V to 5.0 V. The thickness of the oxide layers is estimated to be in the range of 5-20 ML; and the band gap for bulk PdO is reported to be 4.0-5.0 V [25]. The absence of the “bias-voltage” dependence could be explained by the high surface conductivity of oxygen vacancies generated under UHV conditions.

The tip effect can also introduce experimental errors. In fact, the image of an object on the surface might be just tip shape deconvolution. The agglomerates might appear larger in the STM image. No changes of the surface topology and of the surface area were observed when the tip was changed, thus implying this effect was not significant. On the other hand, if the tip cannot follow the contour of the surface, the measured surface area by STM will be in error. The good agreement between the STM data and the $^{18}O$ exchange data (Table 7.1) allows us to rule out this effect as well.

Another important issue is the dependence of the surface area calculated from a STM image as a function of the grid step as discussed by Brown et al. [26]. The x- y-step used in our study was approximately 1 Å (500 × 500 Å with image resolution 512 × 512 lines), two times smaller than the Pd-O bond length (2.02 Å). The proper choice of the grid step
is supported by the comparison with the \(^{18}\)O isotope exchange method as shown in Table 7.1.

### 7.4.2 Oxidation of Pd single crystals

Oxidation of Pd single crystals in low pressure (< 1 Torr, typically < \(10^{-6}\) Torr) \(O_2\) has been studied previously, see for example [16, 17, 20, 27-37]. Chemisorption of oxygen atoms on Pd single crystals results in a \(p(2\times2)\) overlayer with 0.25 ML coverage on Pd(111) [16, 38], \(p(2\times2)\) and \(c(2\times2)\) overlayers on Pd(100) with 0.25 and 0.5 ML coverages, and the reconstructed \(c(2\times4)\) superstructure on Pd(110) with 0.5 ML coverage [17]. The oxygen uptake beyond the saturation coverage could be reached (2.3 ML on Pd(111), 0.8 ML on Pd(100) and 1.8 ML on Pd(110)) by dosing stronger oxidants such as \(NO_2\) [16, 27, 30] or exposing to \(O_2\) at high pressures and temperatures [17, 20, 29]. A surface oxide appears on Pd(111) [16, 20] and Pd(110) [32, 39], which presents a complex crystal structure distinct from that of PdO or the original metallic facets. On Pd(100), the surface oxide appears to have a structure close to PdO(001). It is suggested that PdO forms through a nucleation mechanism [16]. Once the bulk oxide forms, the surface roughens [16, 27].

It is possible that bulk palladium oxide could be formed only when a critical concentration of dissolved oxygen was reached in the near surface region. The formation of this stoichiometric PdO was characterized by the drastically dropped oxygen uptake rate, the complete fading of the metallic Pd(110) LEED pattern, the 0.2-0.7 Pd/O atomic ratio detected by AES and the roughened “cauliflower-like” surface structure imaged by STM [19]. The roughened surface structure with an increase in surface area could be
rationalized as a major lattice expansion during the chemical transformation ‘Pd metal’ → ‘Pd oxide’. The Pd atom density for the oxide is only 60% of the density for the metal structure. In addition, the Pd-Pd nearest neighbor distance is 3.04 Å for PdO, about 10% larger than the 2.75 Å for Pd metal.

The fact that we did not observe any XRD pattern of PdO (Figure 7.1), which should be detectable for the thick PdO layer (2-7 nm estimated from STM images), is an indication that the oxide layer is either amorphous or crystalline with crystallites too small to diffract coherently. The STM images do not reveal preferential growth and thus we conclude that the oxide layer is amorphous. A number of semi-spherical oxide agglomerates were observed in this study (Figure 7.2) possibly due to many nucleation sites of oxide growth. Unfortunately we do not know the nature of these sites. It might be structural defects but most probably this is a fluctuation of the oxygen concentration in the near-surface region, which causes a local transformation Pd→PdO. The mean size of the oxide agglomerates is different on the Pd(111) and Pd(110) surfaces. The most dense Pd(111) surface expanded more than the more open Pd(110) surface. The concentration of dissolved oxygen also might affect the oxide agglomerate size. Oxidation of Pd single crystals including Pd(111), Pd(100) and Pd(110) suggested that the oxygen diffusion from surface to the bulk depends on the surface crystallography with the highest rate of diffusion determined on the open Pd(110) surface. Indeed, the oxygen uptakes were 13 ML, 17 ML and 25 ML on Pd(111), Pd(100) and Pd(110) respectively after exposure to 25 Torr O₂ at 600 K for 10 min [19]. Therefore the Pd→PdO transformation might proceed at a higher bulk oxygen concentration for a given O₂ gas pressure for the Pd(110)
single crystal, resulting in a greater number of nucleation sites. This should lead to smaller agglomerates.

It is interesting to note that the surface area increase after oxidation of a well-annealed metallic supported catalyst agrees with the corresponding result on single crystals (Table 7.2). This is to be expected as metal crystallites on a supported catalyst are composed of low index planes, as shown for example by TEM [40]. Thus, the increase in surface area observed on supported Pd catalysts after oxidation is caused by surface roughening.

### 7.4.3 H₂ reduction

The measurement of surface area for supported Pd catalysts requires reduction of the oxidized sample usually in H₂ before chemisorption. Reduction in H₂ however results in changes of the surface area as demonstrated in Table 7.3. Note that the reduction temperature is an important parameter. Scanning tunnelling Microscopy images of the pre-oxidized Pd(111) and Pd(110) surfaces reduced at a temperature of 673 K demonstrated a fairly smooth surface with clearly visible monatomic steps (Figure 7.4). The surface area after reduction was only about 1.1 times higher than the metal surface area compared to the two-fold increase after pre-oxidation. On a supported catalyst, reduction at high temperatures might also cause Pd sintering. Suh and Park [41] using transmission electron Microscopy (TEM) observed significant sintering of finely dispersed Pd/C catalyst following treatment at 673 K. Logan et al. [13] detected only Rh metal agglomerates with well-defined low index facets after reduction in H₂ at 773 K. At 373 K however, the rate of reduction i.e. the rate of generation of free Pd atoms exceeds the rate of their diffusion and re-crystallization and therefore the surface remains
amorphous. TEM studies by Datye et al. [12] reported the formation of an amorphous Rh metallic layer on crystalline RhO agglomerates during reduction at 323 K in hydrogen. The surface area decreased even after 373 K reduction but it could be due to the collapse of the Pd agglomerates after the PdO→Pd transformation. It is reasonable to assume that the large agglomerates should experience greater shrinking due to the bigger contribution of bulk atoms compared to surface atoms. Thus, the bigger agglomerates collapse more. This might explain why the oxidized Pd(110) surface shows only 24% surface area decrease after H₂ reduction at 373 K, whereas the surface area decreased 42% for oxidized Pd(111).

The main conclusion from the H₂ reduction experiments is that the area of the reduced sample is different from the area of the actual oxidized catalyst.

7.5 Summary

Planar model catalysts: Pd(111) and Pd(110) were used to study palladium oxidation and methane combustion. The surfaces were studied by STM, TPD, XPS, AES and LEED. The advantages of using a model catalyst approach were demonstrated by accurate surface area measurements, which were performed by the surface area integration of STM images and by ¹⁸O isotope exchange. The surface area integration of STM images was performed by triangulation of the STM image based on the x-/y- grid with a 1 Å step. Surface ¹⁶O atoms were exchanged by ¹⁸O atoms in gas phase during ¹⁸O exchange experiments, and the uptake was then measured by TPD. The area measurement by ¹⁸O isotope exchange and by STM image analysis showed similar values.
Exposure of the Pd(111) and Pd(110) single crystals to 100-150 Torr O$_2$ at 600 K led to an increase in surface area by a factor of approximately two. The effect was more pronounced for the Pd(111) surface. This might be because the close packed Pd(111) surface experienced a greater lattice expansion during the Pd$\rightarrow$PdO transformation than the open Pd(110) surface. The other explanation is that because of the higher oxidation rate on the (110) surface, smaller oxide agglomerates were formed due to a higher density of oxide nuclei. The smaller oxide agglomerates on the (110) surface created a lower surface area than the bigger agglomerates in the case of the Pd(111) surface. On both surfaces, oxide agglomerates formed an amorphous structure. A surface with more pronounced “cauliflower-like” structure was observed after treatment of the Pd single crystals in a lean O$_2$ + CH$_4$ reaction mixture.

The H$_2$ reduction of pre-oxidized Pd(111) and Pd(110) crystals resulted in the decrease of surface area of the oxidized Pd(111) and Pd(110) crystals. An amorphous metallic surface was found after reduction at 373 K, whereas an almost smooth surface with area of only 1.1 times that of clean metallic surface was observed after 673 K hydrogen reduction. Characteristic single crystal features were observed by LEED after 673 K reduction in H$_2$. These results underline the importance of the proper choice of reduction conditions prior to surface area measurements.

In conclusion, the surface area of Pd(111) and Pd(110) single crystals changes after they are subjected to O$_2$ oxidation, methane combustion or H$_2$ reduction. The surface area change after oxidation on single crystals agrees with the ones on supported catalysts and it us due to roughening of the PdO surface. These results imply that pre-treatments
before Pd surface area measurement can modify the Pd surface area on supported catalysts.
REFERENCES


Table 7.1  Comparison of surface area determined by STM image analysis (STM) and $^{18}$O isotope exchange ($^{18}$O). Oxidation carried out at 100 Torr O$_2$, 600 K, 10 min and reaction at 600 K, 16 Torr CH$_4$, 160 Torr O$_2$, 624 Torr N$_2$, 60 min.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment Condition</th>
<th>*Surface Area Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(111)</td>
<td>oxidation</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>reaction</td>
<td>3.2</td>
</tr>
<tr>
<td>Pd(110)</td>
<td>reaction</td>
<td>1.6</td>
</tr>
<tr>
<td>Pd foil</td>
<td>reaction</td>
<td>-</td>
</tr>
</tbody>
</table>

* Surface area increase $= \frac{\text{Oxide surface area}}{\text{Metal surface area}}$

** Monteiro et al. [14]
Table 7.2  Surface area increase after oxidation of Pd catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Area Increase</th>
<th>Oxidation condition</th>
<th>Method of measurement</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.5% Pd/Al₂O₃</td>
<td>2.7</td>
<td>973 K, air, 24 hr</td>
<td>H₂-O₂ titration</td>
<td>[10]</td>
</tr>
<tr>
<td>10% Pd/ZrO₂</td>
<td>2.5</td>
<td>973 K, air, 24 hr</td>
<td>H₂-O₂ titration</td>
<td>[10]</td>
</tr>
<tr>
<td>Pd(110)</td>
<td>1.9</td>
<td>600 K, 150 Torr O₂, 30 min</td>
<td>STM image analysis</td>
<td>Present work</td>
</tr>
<tr>
<td>Pd(111)</td>
<td>2.3</td>
<td>600 K, 150 Torr O₂, 30 min</td>
<td>STM image analysis</td>
<td>Present work</td>
</tr>
</tbody>
</table>

*Surface area increase = \( \frac{\text{Oxide surface area}}{\text{Metal surface area}} \)
Table 7.3  Surface area decrease after reduction of preoxidized Pd(111) and Pd(110) evaluated by integration of STM images. Oxidation conditions were 150 Torr O₂ at 600 K for 30 min. Reduction conditions were 1 Torr H₂ at 373 or 673 K for 1 min.

<table>
<thead>
<tr>
<th>Oxidized sample</th>
<th>H₂ reduction temperature</th>
<th>Surface area increase factor*</th>
</tr>
</thead>
<tbody>
<tr>
<td>no reduction</td>
<td></td>
<td>1.9</td>
</tr>
<tr>
<td>Pd(110)</td>
<td>373 K</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>673 K</td>
<td>1.1</td>
</tr>
<tr>
<td>no reduction</td>
<td></td>
<td>2.3</td>
</tr>
<tr>
<td>Pd(111)</td>
<td>373 K</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>673 K</td>
<td>1.1</td>
</tr>
</tbody>
</table>

*Surface area increase factor = \( \frac{\text{Oxide surface area}}{\text{Metal surface area}} \)
Figure 7.1  X-ray diffraction pattern obtained on Pd(111) after oxidation in 150 Torr O$_2$ at 600 K for 30 min. The diffraction peaks corresponding Pd metal were labelled out. No diffraction signal for PdO was detected, for example at 2$\theta$ of 29.3° (100), 33.6° (002) or 33.9° (101).
Figure 7.2 STM images obtained after exposure of Pd(111) (a and b) and Pd(110) (c and d) single crystals to 150 Torr of O₂, at 600 K for 30 min. The sample bias was 1 V, the tunnelling current was 0.5 nA.
Figure 7.3 STM images obtained from Pd(111) (a)-(b) and Pd(110) (c)-(d) surfaces exposed to 16 Torr CH₄, 160 Torr O₂, and 624 Torr N₂ at 600 K for 60 min. The sample bias was 1 V, the tunnelling current was 0.5 nA.
Figure 7.4  STM images obtained after reduction in 1 Torr of H$_2$ of the pre-oxidized Pd(111) (a)-(b) and Pd(110) (c)-(d) surfaces at 373 K (a), (c) and at 673 K (b), (d). Arrows designate the step orientation in (a)-(b), and $<1\bar{1}0>$ in (c)-(d). The sample bias was 1 V, the tunnelling current was 0.5 nA.
Chapter

8 Catalytic Methane Combustion over Pd Single Crystals
Abstract

Catalytic methane combustion was studied over palladium single crystals: Pd(111), Pd(100) and Pd(110) at 600 K in excess oxygen \((O_2:CH_4 = 1:10)\). Stoichiometric palladium oxide was formed with an increase in the surface area by a factor of approximately two under the lean reaction condition. The oxide phase presented “cauliflower-like” surface structure composed of approximately 4 nm sized semispherical oxide agglomerates, not correlating to the original single crystal orientation. The turnover rates were 0.72 s\(^{-1}\) on Pd(111), 0.9 s\(^{-1}\) on Pd(100) and 0.9 s\(^{-1}\) on Pd(110) at 600 K, 160 Torr O\(_2\), 16 Torr CH\(_4\), 1 Torr H\(_2\)O and N\(_2\) balance to 800 Torr, suggesting that the methane combustion reaction was structure insensitive over the oxidized single crystal catalysts. Methane combustion on palladium single crystals experienced an activation period in which the initial nominal turnover rates based on the metal surface area were only about 1/8-1/4 of the steady-state rates based on the oxide surface area. This activation period was induced by the slow oxidation of palladium single crystals and the surface area increase during the reaction. The increase in the surface area happened mostly in the first 10 min of the reaction and then leveled off. Carbon dissolution into palladium bulk was found during methane combustion under reaction condition in excess methane \((CH_4:O_2 = 10:1)\) but not in excess oxygen. Removal of the dissolved carbon required cycles of high-pressure oxygen exposure, for example 1 Torr at 780 K, followed by flashing at high temperature up to 1000 K.
8.1 Introduction

Methane, CH₄ is the ‘greener’ of the fossil fuels. It has the highest hydrogen to carbon ratio of all hydrocarbons and thus could produce the highest amount of energy per CO₂ formed when it is burned. Combustion of methane could be achieved through conventional flame combustion in the gas phase or via catalytic reaction on catalyst surface referred as catalytic methane combustion. As compared with the flame combustion, catalytic combustion takes the advantage of the catalyst that lowers the activation energy to break the C-H bond and thus reduce the operating temperature. This advantage becomes more and more economically and environmentally valuable with the increasingly stringent regulation for the emission level of NOₓ, which is generated thermally in gas-fired turbines.

Palladium has proven to be the best catalyst for catalytic methane combustion because it has the highest turnover rate (TOR) as compared to other metals [1]. A question of practical and scientific interest regarding methane combustion on Pd-based catalysts is the reaction catalyst-structure sensitivity. In other words, does the TOR for methane combustion change as the structure of the catalyst is changed? A catalytic reaction is referred to as structure sensitive if the TOR under fixed conditions depends on surface crystalline anisotropy as expressed on clusters of varying sizes especially in the range of 1 to 10 nm or on single crystals exposing different faces [2, 3]. The structure sensitivity of methane combustion on palladium does not have a unanimous answer. Baldwin and Burch [4, 5] found that the TOR changed by two orders of magnitude on a series of Pd/Al₂O₃ catalysts with no correlation between the particle size and TOR. Note that the
catalysts used in their study were prepared from two different kinds of palladium sources: palladium chloride and palladium nitrate. The chlorine deposited on the catalyst surface during preparation could inhibit the methane combustion reaction [6] and cause the wide range of TOR. Hicks et al. [6, 7] reported higher TOR for larger Pd crystallites. Based on the observation that small Pd crystallites were converted into dispersed PdO while large crystallites were converted into small crystallites covered with adsorbed oxygen, they concluded that the extent of palladium oxidation depended on agglomerate size, and the fully oxidized PdO phase on small crystallites was less active than the adsorbed oxygen overlayer on large Pd crystallites. This conclusion was however at odds with those reported by Carstens et al. [8] and Burch and Urbano [9] who found that chemisorbed oxygen was either inactive or not as active as fully oxidized palladium for methane combustion. Garbowski et al. [10] proposed that the reaction was structure sensitive since higher activation was found on less packed planes like Pd(110) and Pd(100) than on the more packed Pd(111). In contrast, Cullis and Willatt [11] did not observe strong effects of crystallite size on reaction turnover rate. Ribeiro et al. [12] found that for catalysts with different supports and prepared with different metal precursors, the rates were the same in the agglomerate range from 2 nm to 10 nm. Most recently, Fujumoto et al. [13]on Pd/ZrO2 and Müller et al. [14, 15] on Pd-Zr alloys found a “weak” structure sensitivity as agglomerate size varied. The turnover rate increased by a factor of 6 [13] and 7 [14] with increasing Pd crystallite size from 3 to 9 nm [13] and from 6 to 12 nm [14].

Noteworthy that this structure sensitivity issue has been addressed on supported catalysts in most of the literature work summarized above. A number of non-related factors were
entangled because of using the supported catalysts. These factors, including support-catalyst interaction [14], catalyst activation and deactivation by impurities [4], catalyst oxidation states [6, 7], and the spreading of oxide phase over the supports [16, 17] during reaction, are in general difficult to be identified individually. Moreover, it is always difficult to measure the catalyst surface area on supports, so the TOR reported are normally not area corrected.

In this study, we proposed to address the sensitivity issue on palladium single crystal model catalysts. The reaction kinetics was studied on Pd(111), Pd(100) and Pd(110) under fuel lean condition (CH$_4$:O$_2$ = 1:10) at 600 K where PdO was the active phase. Compared with supported catalysts, single crystal catalyst has unique advantages. It is free of impurities, has no support effects and no internal heat and mass transfer limitations; in addition, it is easy to track the surface area change during methane combustion with surface science techniques [18]. This single crystal method has been successfully used to identify the structure sensitivity for ammonia synthesis over iron catalysts and ruthenium catalysts [19, 20].

Methane combustion over supported palladium catalysts often experiences an activation period before a steady state reaction rate is reached. In the literature, this behavior has been suggested due to the presence of impurities [21, 22], the interaction with supports [23], the transformation between different sample oxidation states [6, 7], or the morphology change of Pd crystallites [4, 5, 23]. In this study, an activation period was observed in which the initial turnover rate for methane combustion on palladium single crystals was only about 1/8-1/4 of the steady-state rate. This lower initial reaction rate
was attributed to the low PdO formation rate on Pd single crystals and the surface area increase during palladium oxidation.

It is suggested that carbon diffuses in palladium bulk after an exposure to carbon sources and might affect the activity of palladium catalysts [24, 25]. The dissolved carbon forms a Pd-C solid solution also referred as PdC\textsubscript{x} phase. The content of carbon could reach as high as 13-15% after an exposure of palladium in an atmosphere of C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{2} or CO [26, 27]. Other procedures, such as deposition of Pd agglomerates on carbon supports [24, 28] or evaporation of Pd on carbon thin film substrates [29] would result in the carbon dissolution as well. The dissolved carbon occupies the metal octahedral sites [25, 27] and expands the crystal structure. The Pd lattice parameter determined by X-ray Diffraction (XRD) is increased by about 2.8% with 13% carbon incorporation [30]. Even trace amount of carbon on Pd(110) surface could cause an outward expansion of the inter-planar spacing about 4% for the first 3-4 surface layers [29]. The presence of carbon both on the palladium surface and in the bulk has profound effects on the catalyst activity. Ellipsometric studies by König et al. [31] and Graham et al. [32] reported the growth of highly porous PdO layers upon methane combustion under rich condition (CH\textsubscript{4}:O\textsubscript{2} = 1.5:1) comparing with the dense layers formed under lean condition (CH\textsubscript{4}:O\textsubscript{2} = 1:4). It is also found that carbon dissolution could suppress the chemisorption of hydrogen, oxygen and CO, reduce the ability to form palladium hydride (\(\beta\)-PdH\textsubscript{n}), increase the heat of adsorption for hydrogen on Pd, while reduce that for CO [25, 28]. The recovery of the clean palladium phase from carbon contaminations is suggested to be achieved by heating in inert atmosphere at 870 K or in vacuum at 600 K [27, 30], in
reduced atmosphere for example H₂ at 420 K [27, 33], or in oxidized atmosphere (O₂) at 420 K [27, 28].

Carbon is also found to dissolve into palladium during catalytic methane combustion on a Pd polycrystalline foil under fuel rich condition (CH₄:O₂ = 10:1) [34]. After the treatment, the Pd foil had a significant surface area increase of 18-fold compared to the 2-fold increase under lean condition (CH₄:O₂ = 1:10) [34, 35].

To seek for the conditions at which carbon dissolution occurs during catalytic methane combustion over Pd single crystal catalysts, in the present work, labeled methane (¹³CH₄) was used as a reactant and all the ¹³C containing species including ¹³CO and ¹³CO₂ were traced to avoid the interference from ¹²C containing impurities originally present in the reaction system. A direct consequence of this study is to check whether the reaction kinetics obtained for catalyst structure sensitivity study are erased by carbon deposition.

8.2 Experimental Methods

The experiments were carried out in a specially designed system, which consisted of three chambers: ultra-high vacuum (UHV) analysis chamber, UHV Scanning Tunneling Microscopy (STM) chamber and high-pressure reaction cell. The analysis chamber housed facilities for X-ray Photoelectron Spectroscopy (XPS), Auger-electron Spectroscopy (AES), Low Energy Electron Diffraction (LEED), and Temperature Programmed Desorption (TPD). The STM chamber accommodated an ambient-temperature UHV STM (RHK, Inc.). The base pressure in the UHV chambers was 5 × 10⁻¹⁰ Torr (1 Torr = 133.3 Pa). The catalytic CH₄ combustion reaction was carried out in the high-pressure reaction cell (base pressure 2 × 10⁻⁸ Torr). The sample could be
transferred between the chambers, without exposure to the atmosphere, by means of a 142 cm transport arm.

Palladium single crystals: Pd(111) (0.8 mm thick × 7.2 mm diameter), Pd(100) and Pd(110) (both 1 mm thick × 8.5 mm diameter) all made by Princeton Scientific Corp. with mis-alignment < 0.5°, were used as planar model catalysts. The single crystals were mounted on commercial sample holders (RHK, Inc.). The temperature was measured by a chromel-alumel thermocouple spot-welded onto the side of the sample. In the analysis chamber, the sample was heated by electron-bombardment from the rear. In the reaction chamber, the sample was heated by an IR lamp.

The temperature programmed desorption spectra were collected at a constant heating rate of 5 K s⁻¹. The oxygen uptake was calculated by integrating the area under the TPD peak and measured in monolayers (1 monolayer = 1 ML = 1.53 × 10¹⁵ atoms cm⁻² on Pd(111), 1.32 × 10¹⁵ atoms cm⁻² on Pd(100) and 0.94 × 10¹⁵ atoms cm⁻² on Pd(110)) by comparing to standard calibration values [36-38].

Scanning tunneling microscopy images were obtained using Pt-Ir tips electrochemically etched in NaCl/NaNO₃ melt at around 400-450 °C. The surface area was then calculated by taking discrete image pixels and joining them by a series of 3D oriented triangles. Integration of the area of individual triangle gives the total area [39].

The crystal cleaning procedures consisted of cycles of Ar⁺ sputtering at room and elevated temperatures, annealing in UHV, exposure to O₂ and NO₂ followed by flashing at 1000 K for Pd(100) and Pd(110) and 1100 K for Pd(111) for 60 seconds in UHV. The
sample cleanliness was checked by TPD, AES and LEED. The NO₂ and O₂ gases were introduced into the analysis chamber through a capillary doser.

The methane combustion reaction on Pd single crystals was performed in the high-pressure reaction cell 615 cm³ in volume in a batch mode. The reaction gases were introduced from a gas manifold in the following order: N₂ (624 Torr), O₂ (160 Torr), and CH₄ (16 Torr) for combustion under lean condition and N₂ (624 Torr), CH₄ (160 Torr), and O₂ (16 Torr) for combustion under rich condition. For labeled methane (¹³CH₄) experiments, ¹³CH₄ was inlet into the reaction cell instead of CH₄. The reactants were mixed for 30 min before reaction by a circulation pump model MB-21 (Metal Bellows, Inc.) at a nominal rate of 1000 cm³ min⁻¹. This circulation was continued throughout the reaction to effectively eliminate external mass transfer limitation [35]. Reaction was normally carried out at 600 K for 60 min with about 2.5% of the CH₄ being consumed under lean condition and about 3% for rich condition. The reaction mixture was analyzed with an Agilent 6890 Series gas chromatograph (GC) using a thermal conductivity detector, and a 15-ft Carboxen 1000, 60/80 mesh column.

The ¹⁸O isotope exchange experiment to measure the surface area change on Pd single crystals after CH₄ combustion was also performed in the high pressure reaction cell following the procedure described before [35]. Briefly an oxidized palladium sample was exposed to 5 Torr ¹⁸O₂ at 600 K for 12 s, and the uptake of ¹⁸O exchanged was then measured by TPD analyzing all gases containing labeled oxygen.
8.3 Results

8.3.1 Characterization of Pd single crystals before and after reaction

The state of Pd single crystal surface was examined by LEED, AES, XPS, TPD and STM before and after catalytic methane combustion under standard lean condition. Before reaction, only features corresponding to metallic Pd could be observed. LEED revealed clear single crystal structure with sharp diffraction spots. STM showed smooth surface with terraces separated by monoatomic steps. No Pd single crystal LEED pattern was however observed after reaction except for the bright background. The AES spectrum after reaction revealed two additional peaks at 490 and 510 eV characteristic of oxygen with the O/Pd atomic ratio of approximately 0.7. This lower value than the 1:1 stoichiometric ratio was due to electron beam decomposition of the oxide, with the oxygen desorbing as O\textsubscript{2} [35, 40]. In the XPS spectrum after reaction, the core level Pd 3d\textsubscript{5/2} peak was located at 336.8 eV, shifted 1.8 eV from metallic palladium (335.0 eV), characteristic of PdO. The oxygen uptakes on the Pd(111), Pd(100) and Pd(110) surfaces determined by TPD were 22 ML, 24 ML and 27 ML, respectively. All these results indicated the existence of a stoichiometric PdO layer on the single crystal surface.

Scanning tunneling microscopy images obtained on Pd(111), Pd(100) and Pd(110) after the methane combustion treatment in excess O\textsubscript{2} are presented in Figure 8.1. The three oxidized single crystals showed a similar amorphous PdO surface morphology, not correlating with the original orientation. A clear “cauliflower-like” structure 20 ± 5 nm in size appeared on the Pd surfaces. These large domain structures composed of small semi-spherical oxide agglomerates around 4 nm in diameter.
8.3.2 Surface area measurement

The Pd single crystal surface area increase after methane combustion under standard lean condition was determined by STM image analysis and $^{18}$O isotope exchange. Detailed description of these two methods was the subject of another publication [39]. Table 8.1 summarizes the results. It was found out that the two proposed methods agreed within ±20%. In addition, the two methods provided consistent results with the measurement of the surface area of a polycrystalline Pd foil following methane combustion in excess $O_2$ [35] which is listed in the last row in Table 8.1.

8.3.3 Structure sensitivity of reaction on oxide phase

In this study, the structure sensitivity for catalytic CH$_4$ combustion was addressed only on the oxide phase, which was the thermodynamically stable phase under the reaction conditions [41-43]. Before the measurement of the reaction kinetics, blank experiment was performed to test the background activity of the reaction cell. A stainless steel foil with the same size as Pd single crystals was mounted on a standard RHK sample holder and exposed to the standard lean methane combustion atmosphere at 600 K for 60 min. No activity was detected with the gas chromatograph suggested a negligible background contribution.

The turnover rates on the three Pd single crystals were calculated from the reaction rate divided by the surface area. Here, the reaction rate is defined as the methane conversion per reaction time. Assuming the reaction order for CH$_4$ is 1, for H$_2$O is −1 (reaction is inhibited by water), and 0 for both $O_2$ and CO$_2$, the square of methane conversion ($X^2$)
could be derived to have a linear relationship with the reaction time \( t \) in batch reactor [35].

\[
X^2 = C \cdot t
\]  

The reaction rate is then obtained by solving the constant \( C \), which is the slope for the curve \( X^2 \) vs. \( t \). The typical plot for Pd(111) and Pd(100) is shown in Figure 8.2, in which the number of turnovers is defined as:

\[
Number \ of \ turnovers = \frac{N_0 \cdot X}{S_A \cdot D_A}
\]  

\( N_0 \) is the total number of CH\(_4\) molecules in the reaction cell before the combustion, \( S_A \) is the surface area of Pd single crystal and \( D_A \) is the Pd atom surface density on the single crystals.

It is noted that the single crystal catalyst was not fully activated at the early stage of the reaction. An activation period was observable in the first 5 min (Figure 8.2). The reaction rate was therefore determined from the constant slope where steady state activity was reached.

Based on the PdO surface area determined by STM image analysis (Table 8.1), the turnover rates for catalytic methane combustion over Pd single crystals are 0.72 s\(^{-1}\) on Pd(111), 0.9 s\(^{-1}\) on Pd(100) and 0.9 s\(^{-1}\) on Pd(110) as shown in Table 8.2. The reaction condition was corrected to 600 K, 160 Torr O\(_2\), 16 Torr CH\(_4\) and 1 Torr H\(_2\)O. The fact that almost identical turnover rates were obtained on oxidized Pd(111), Pd(100) and Pd(110) is an indication that methane combustion may not be sensitive to the structure of the oxide.
Table 8.3 summarizes literature turnover rates obtained on supported catalysts and palladium black mostly in the critical range of 1-10 nm [12-15, 35]. The listed turnover rates were corrected to the same condition as in Table 8.2 to provide a proper comparison with obtained on Pd single crystals. One can see from the two Tables that the turnover rate on Pd single crystal was generally higher than on supported catalysts, indicating the existence of the effect of impurities or interaction with supports on supported catalysts.

After each catalytic reaction, the structure of single crystals was checked with LEED to verify the consistency throughout the treatment. Clear Pd single crystal (1×1) pattern with sharp integral spots was observed after sample cleaning with temperature programmed desorption. Therefore, the single crystal structure remained unchanged after methane combustion at 600 K.

8.3.4 Catalyst activation

Palladium single crystal experienced an activation period during methane combustion as shown in Figure 8.2. The initial turnover rate, assuming a constant slope during the first 5 min (see Figure 8.2) and a constant surface area as of the metal surface, was around 1/5 of the steady state turnover rate on Pd(111), 1/8 on Pd(100) and 1/4 on Pd(110). Activation period has also been reported on supported Pd catalysts [4, 6, 7, 21-23]. Some hypotheses have been raised to explain this time-dependent behavior, such as the presence of impurities [21, 22], the interaction with supports [23], the morphology change of Pd crystallites [4, 23] or the transformation between different sample oxidation states [6, 7]. The possibility of impurity presence on single crystal surface to block catalytic sites could be ruled out by both XPS and AES, which did not detect any
noticeable amount of impurities for example SiO$_2$, before and after the reaction. There is no catalyst-support interaction for single crystal. Although the surface morphology changed during the reaction with an increase in the surface area due to the formation of PdO, the lower initial TOR could not be solely attributed to the area enhancement because a maximum factor of three was determined for the surface expansion on Pd single crystals under reaction condition (see Table 8.1). Therefore, the slow transformation from Pd metal to Pd oxide on Pd single crystals is proposed as a cause of the catalyst activation, since Pd metal is known to present no activity for methane combustion at low temperatures [8, 44].

To test this hypothesis, experiments were carried out to oxidize Pd single crystals in high pressure O$_2$ (1-150 Torr) at 600 K for various reaction durations [45]. It was found that a fresh single crystal would not be fully oxidized at the early stage of oxidation [45]. Exposure of a Pd(110) surface to 150 Torr O$_2$ at 600 K, bulk oxide was not formed in the first minute and the surface presented a semi-ordered structure with small agglomerates around 1.5-2 nm in diameter growing along the $<1\bar{1}0>$ direction (Figure 8.3). In addition, LEED revealed a weak streaky Pd(110) (1×1) pattern. The surface area increases were estimated to be only 1.2 after the treatment.

Further support to this hypothesis came from the comparison between methane combustion under standard lean condition over clean Pd single crystal and over preoxidized Pd single crystal in 150 Torr O$_2$ at 600 K for 60 min. No catalyst activation was observable on the preoxidized Pd(100) as shown in Figure 8.4.
8.3.5 Catalyst oxidation

The fact that a straight line was obtained in Figure 8.2 after the activation period suggested that although Pd single crystal was constantly being oxidized under the reaction condition in excess O\textsubscript{2}, the major surface expansion due to oxidation should happen in the early stage of reaction and then the surface area increase leveled off; otherwise, the reaction rate would have increased with time.

To test this hypothesis, the oxygen uptake and surface area increase were determined on Pd(110) after different methane combustion duration of 10 and 60 min. The result is listed in Table 8.4. Consistent with the observation during oxidation of Pd(110) in high pressure (1-150 Torr) O\textsubscript{2} [45], the amount of oxygen uptake during CH\textsubscript{4} combustion increased with the time of reaction, being 17 ML at 10 min and 27 ML at 60 min. The 1.5 and 1.6 surface area increases after 10 min and 60 min of reaction were compatible. Thus the difference in the reaction rate due to surface area change could be negligible after 10 min of the reaction.

8.3.6 Carbon dissolution

Temperature programmed desorption of O\textsubscript{2} (mass 32), CO (mass 28) and CO\textsubscript{2} (mass 44) on a Pd(100) single crystal after methane combustion under standard lean condition is shown in Figure 8.5(a). The O\textsubscript{2} desorption peaked at 780 K, consistent with the TPD obtained after oxidation of Pd(100) in 160 Torr O\textsubscript{2}, at 600 K for 60 min (Figure 8.5(b)). The amounts of oxygen uptake after CH\textsubscript{4} combustion reaction and Pd oxidation in O\textsubscript{2} were the same and corresponded to 24 ML.
Both CO and CO$_2$ desorption occurred at two different temperatures. The lower temperature desorption peak for CO$_2$, located at 450 K, was about two times as intense as the higher temperature peak at 810 K. The integral of the desorption peaks was equivalent to 0.3 ML and 0.12 ML of CO$_2$ at 450 K and 810 K, respectively. Similarly, the desorption of CO occurred at 580 K and 810 K, with the intensity for the 580 K peak about two times of the peak intensity at 810 K. The integral for CO desorption peaks corresponded to 0.1 ML and 0.05 ML at 580 K and 810 K.

It has been suggested that the carbon desorbed at 450 K and 580 K in the form of CO$_2$ and CO did not come from methane deposited during reaction since the desorption temperature was lower than the reaction temperature of 600 K [35]. Additional support to this conclusion came from the TPD for CO and CO$_2$ after Pd(100) oxidation in 160 Torr O$_2$ as shown in Figure 8.5(b). The low temperature CO and CO$_2$ desorption also appeared and both peaked at 540 K. Besides the 540 K low temperature peaks, high temperature CO and CO$_2$ desorption peaks were observable in Figure 8.5(b) to both locate at 760 K after the Pd(100) oxidation in O$_2$ with the nominal coverage of 0.1 ML of CO$_2$ and 0.05 ML of CO.

The CO and CO$_2$ desorption at high temperature of 810 K after methane combustion (see Figure 8.5(a)) should not relate to CH$_4$ deposition either, because the desorption peaks were of the same intensities as the 760 K peaks obtained after Pd(100) oxidation in 160 Torr O$_2$ (Figure 8.5(b)). The TPD result in Figure 8.5(b) suggested that the Pd(100) single crystal was contaminated by dissolved carbon. This carbon impurity presented mainly in the bulk phase, so a carbon-free surface was available after cleaning cycles in analysis chamber. However, extensive oxidation for example in high pressure O$_2$ at
elevated temperatures could segregate the carbon species to the surface again and then desorbs as CO₂ and CO associated with O₂ desorption during temperature programmed desorption.

To differentiate the effect of carbon impurities originally present in Pd(100) with the influence of methane combustion, labeled methane (¹³CH₄) was used as a reactant to replace ¹²CH₄. Pre-experiment was performed by monitoring the desorption of ¹³C containing species including ¹³CO (mass 29) and ¹³CO₂ (mass 45) after oxidation of Pd(100) in 160 Torr O₂ at 600 K for 60 min. No desorption was observable as shown in Figure 8.5(b) ensured the sample was ¹³C-free. ¹³CH₄ combustion was carried out under the standard lean condition. The TPD result on the single crystal catalyst after the reaction was shown in Figure 8.5(c). No signal from ¹³CO and ¹³CO₂ could be detected, which implied that the amount of carbon deposited on the surface during combustion reaction in excess O₂ was beyond the lowest limitation of our mass spectrometer. Noteworthy that the intensities for CO and CO₂ desorption peaks remained unchanged in Figure 8.5(a) through (c); the integral of the desorption peaks in Figure 8.5(c) was equivalent to 0.09 ML CO₂ and 0.07 ML CO at 810 K.

The TPD result was quite different after methane combustion under standard rich condition (Figure 8.5(d)). Both CO and CO₂ desorption peaks at high temperature of 780 K intensified, corresponding to 0.15 ML CO and 0.75 ML CO₂. The fact that the intensity for the CO₂ peak was about seven times of that obtained after reaction in excess O₂ and Pd oxidation in O₂ was an indication that some carbon incorporated into the bulk structure of the palladium oxide during the treatment in excess methane.
Recovery the clean palladium phase from carbon incorporation is very difficult, requiring extensive cleaning. It took us about two months, more than 300 cycles of high-pressure O₂ oxidation (1 Torr O₂ at 780 K for 10 min) and 300 cycles of Ar⁺ ion sputtering followed by O₂ or NO₂ dosing at 550 K to remove the dissolved carbon in a Pd(110) single crystal after five runs of CH₄ combustion under rich condition. The high-pressure oxygen oxidation was found to be more effective than sputtering or O₂ dosing to clean off carbon impurities.

8.4 Discussion

8.4.1 Reaction structure sensitivity on oxide phase

To identify whether a reaction is sensitive to the structure of the catalyst, one need to compare the reaction turnover rates on a set of catalysts with the size for the catalyst crystallites varying especially in the range of 1-10 nm [2, 3]; or alternatively, compare the rates on a set of large single crystal surfaces as the nanometer sized catalyst crystallites are formed by a combination of single crystal surfaces [2, 3]. The latter approach has been used to confirm the structure sensitivity for ammonia synthesis on iron catalysts [19], and the structure insensitivity for oxidation of carbon monoxide on platinum catalysts [46]. In this study, this single crystal approach was used to investigate the structure sensitivity for methane combustion on palladium oxide. Since single crystals of PdO with different orientations cannot be prepared by the standard cutting and polishing techniques, we proposed to use the metallic planes Pd(111), Pd(100) and Pd(110) to simulate the most common faces on a metal crystallite and then measure the rates as well as the surface areas after they oxidize. It is expected that the same type of oxide
structures would be available on a supported catalyst. The fact that same turnover rates were obtained on different palladium single crystal surfaces not correlating to the original orientations is an indication that the complete combustion of methane over oxidized Pd single crystals is catalyst structure independent. Indeed, under the standard catalytic reaction condition in excess O₂, stoichiometric palladium oxide was formed, which however did not grow epitaxially with the single crystal substrate. The consequence is that amorphous PdO was formed and present similar “cauliflower-like” surface structures composed of semispherical oxide agglomerates around 4 nm in size (Figure 8.1). The formation of stoichiometric PdO was characterized by the complete fading of the Pd single crystal (1×1) LEED pattern, the 0.7 O/Pd atomic ratio detected by AES and the 1.8 eV core level Pd 3d₅/₂ peak position shift to higher energy observed with XPS.

In contrast to the growth of amorphous PdO, the TEM studies by Lyubovsky et al. [47] and the in-situ Raman studies by Carstens et al. [8] suggested the formation of crystalline PdO during oxygen oxidation or catalytic methane combustion of Al₂O₃ and ZrO₂ supported Pd catalysts. The conflict with the literature results could be understood by the Raman observation by Su et al. [48] who reported that during oxidation of a Pd/Al₂O₃ supported catalyst in O₂ atmosphere, an amorphous oxide film was formed initially which then underwent a slow crystallization process. The transformation from the amorphous film to crystalline oxide involves an activation barrier with a higher rate at a higher temperature; and it was determined using in-situ Raman that only 7% PdO was crystallized during oxidation at 533 K [48]. Even oxidizing a Pd/Al₂O₃ catalyst at a temperature of 1043 K in 1 atm air, the Transmission Electron Microscopy (TEM) studies by Datye et al. [49] showed a bulk single crystal PdO phase had a surface layer of
amorphous oxide. Thus, the appearance of only amorphous oxide on the surface in our study might be attributed to the low reaction temperature of 600 K.

The structure sensitivity for methane combustion on Pd catalysts was proposed by Garbowski et al. [10] based on the argument that PdO with tetragonal lattice structure was able to epitaxially form on top of the less packed square (100) plane and rectangle (110) plane; whereas oxidation of dense hexagonal (111) plane occurred with profound metal reorganization, thus required extra activation energy [10]. This argument is somehow not complete since in order to grow an epitaxial film, a close lattice match with the substrate to minimize the interfacial strain, compression or relaxation depending on the lattice parameters $a_{\text{film}}$ $(a_{\text{sub}}$ is crucially required [50]. Thus, the observation of amorphous palladium oxide phase on the single crystal surfaces could be rationalized by the over 24% lattice misfit between PdO and Pd(111), Pd(100) or Pd(110). Even, for example under some particular condition, the interfacial strain due to the lattice non-commensurability were relieved, and an epitaxial oxide film was grown for the first few layers, the rapid accumulation of the strain energy with the film thickness due to the inherent stiffness of the oxide would exaggerate the misfit dislocation, resulting in the film buckling, the formation of 3D islands and the ultimate morphological transformation to amorphous oxide [50, 51]. As the heterogeneous catalytic reaction occurs only on the surface of catalysts, it is not critically important to understand whether there exists crystalline PdO phase in the bulk concealed by the surface amorphous phase.
8.4.2 Catalyst activation

This research has demonstrated that methane combustion on palladium single crystal catalysts under standard lean condition experienced an activation period. The activation was observed to occur in 5 min after the beginning of the reaction. A previous study from our group however showed almost no activation period for methane combustion over a Pd polycrystalline foil [35]. Since Pd metal is known to present no activity for methane combustion at low temperature [8, 44], this different activation behavior on the two types of model catalysts could be attributed to the higher PdO formation rate on foils than on the single crystals. Studies on oxidation of Pd single crystals in high pressure O$_2$ (1-150 Torr) suggested that the palladium oxidation proceeds through a three-step mechanism [45]. Namely, (1) O$_2$ dissociatively adsorbs on Pd surface; (2) atomic oxygen diffuses into metal near surface region and bulk; (3) stoichiometric PdO forms. The oxygen species diffused in the palladium near surface region is likely the precursor to bulk oxidation [45]. The concentration of oxygen increases as the oxygen atoms diffuse into Pd metal continuously. At a certain critical concentration, the bulk oxide phase nucleates and grows [45]. It is expected that the oxygen diffusion from surface to bulk depend on the surface perfection of the crystal. A better dissolution should be found on a step or defect site. Thus, a higher density of oxide nucleation was observed in the vicinity of the steps on Pd(111) and Pd(100) surfaces, and on a Pd(110) surface initial oxide nucleation was found to along the steps in the $<1\bar{1}0>$ direction [45]. Compared with the single crystal samples, which have the step and defect density estimated to be less than 1%, Pd polycrystalline foil presents a large number of steps, kinks and defects created by gain boundaries on the surface, which act as active oxygen adsorption and
penetration sites, and therefore lead to a higher oxidation rate. In fact, an equivalent of 55 ML of PdO was formed on a Pd foil after 3 min of the CH₄ combustion in the standard lean condition [35]. The oxygen uptakes were 60 ML and 85 ML at 10 min and 60 min of the reaction on the Pd foil respectively [35]. In comparison, the oxygen uptakes on Pd single crystals were in the range of 22-27 ML after 60 min of the CH₄ combustion in excess O₂. The much higher oxygen uptake amount obtained on Pd foil than on Pd single crystals (Table 8.4), in combination with no activation period is an indication that the oxidation of Pd foil is faster compared with the catalytic reaction; whereas, methane combustion might occur on a not fully oxidized Pd single crystal surface in the initial stage.

It is generally believed that a monolayer of oxygen is rapidly adsorbed on the palladium surface under the reaction condition [9]. If chemisorbed oxygen were more active than the oxide phase [6, 7], we would expect a higher activity in the initial stage of the reaction. Instead, a lower activity was observed in this study, which further supports the conclusion by Carstens et al. [8] and Burch and Urbano [9] that chemisorbed oxygen is either inactive or not as active as oxidized palladium for CH₄ combustion.

Baldwin and Burch [4, 5, 23] reported an increase in the activity of supported catalysts with time on stream under reaction conditions and assigned the activation to the changes in the surface morphology and surface structure of palladium crystallites. Some hypotheses have been raised to explain this surface reconstruction [23], among which a typical explanation was the deposition of carbon that might re-order the surface of the palladium oxide [4, 23]. In this study, it was also found that the palladium single crystal surfaces were roughened with an increase in the surface area by a factor of approximately
two under the reaction condition in excess oxygen (Figure 8.1 and Table 8.1). This observation was rationalized as a major lattice expansion during the chemical transformation ‘Pd metal’ → ‘Pd oxide’ [39]; but not due to the existence of carbon, since no evidence was revealed (Figure 8.5(c)) in our work for carbon deposition or dissolution during methane combustion in excess oxygen. The CO and CO₂ desorption associated with O₂ desorption at 760-810 K (Figure 8.5(a) and (b)) was assigned to the dissolved carbon impurities originally present in the single crystal samples. Thus at least in the reaction system we are studying, there is no carbon deposition that might modify the surface structure and consequently the catalyst activation. It should also be noted that the possibility of dissolved carbon effect on the reaction kinetics obtained for catalyst structure sensitivity study is excluded.

8.4.3 Carbon dissolution

The dissolution of carbon in palladium bulk has been studied previously on Pd single crystals [29], foils [34, 35], supported catalysts [4, 23-25, 33, 52, 53], Pd film [31, 32] and Pd black [26, 27]. It is generally believed that the dissolution process involves deposition of a carbonaceous overlayer, followed by an activated diffusion of carbon atoms through the Pd metal lattice [27]. Thus, the extent of carbon incorporation is determined by the surface coverage of deposited carbon species as well as the bulk diffusion rate. The carbon concentration on Pd metal surface depends on a number of factors including: (1) The perfection of palladium crystals [26, 29, 33, 35, 52] as chemisorption prefers to occur at defect sites [54]. The formation of PdCₓ phase by carbon diffusion is suggested to facilitate on small Pd crystallites with high density of defects [26, 33, 52]; whereas, single crystals or foils are expected to present much less
amount of interstitial bulk carbon [35]. (2) The dissociative adsorption of precursor carbon species. Compared with the unsaturated hydrocarbons such as C_2H_4 and C_2H_2 [26, 27, 33], the Pd-C phase appears at higher temperature for the saturated hydrocarbons such as CH_4, which is difficult to dissociatively adsorb on Pd surface [55]; and for CO, which does not undergo dissociative chemisorption but only breaking the C-O bond at high temperature [4, 23, 27, 31, 32, 35]. (3) The carbon precursor gas phase concentration [31, 32, 34, 35]. On a Pd polycrystalline foil and a thick Pd film, the carbon dissolution is only found during methane combustion in excess CH_4 but not in excess O_2 [31, 32, 34, 35]. (4) The substrate temperature [27]. There should exist an optimum substrate temperature for carbon dissolution since chemisorption is an exothermic process, increasing the Pd metal temperature would shift the balance to desorption and therefore lower the carbon species surface coverage; on the other hand, the diffusion of carbon atoms into bulk is activated at high temperature, which recovers the occupied adsorption sites and facilitates further chemisorption.

We have shown in this study the evidence for carbon dissolution in palladium single crystals during methane combustion under standard rich condition but not under lean condition from TPD spectra (Figure 8.5). Based on the discussion above, we could try to qualitatively explain the different carbon dissolution behavior in excess O_2 and in excess CH_4. Methane is one of the most difficult compounds among all the hydrocarbons in terms of C-H activation [55]. The dissociative chemisorption of methane on Pd metal is suggested to follow a direct dissociation mechanism, with the dissociation probability decreasing linearly with increasing oxygen coverage and reaches almost zero on an oxygen-covered surface [56, 57]. The consequence is that the actual CH_4 dissociative
adsorption rate equals to the CH₄ combustion rate. In other words, any carbon deposition is burned in excess O₂ during methane combustion. On the other hand, the situation could be slightly different in excess CH₄. It has been proposed that the kinetics of methane combustion at low temperature is consistent with the Mars-van Krevelen-redox mechanism, in which CH₄ is oxidized by the lattice oxygen in PdO and the reduced Pd catalyst is subsequently reoxidized by gas phase oxygen [58-60]. Assuming that in a strong reducing atmosphere for example in our case with excess CH₄(CH₄:O₂ = 10:1), Pd metal phase could be locally stable for a reasonably short period of time allowing the chemisorption of CH₄ to occur on the metal phase. Due to the extremely higher CH₄ adsorption rate on Pd metal than on Pd oxide [56, 57], the concentration for dissociated CH₄ could be much higher on the local metal surface than on the oxide surface, which then leads to the carbon diffusion into palladium bulk through the metal lattice.

8.5 Summary

The catalytic combustion of methane in excess oxygen (O₂:CH₄ = 10:1) was studied at 600 K over palladium single crystals: Pd(111), Pd(100) and Pd(110), which were expected to simulate the most common faces on a metal crystallite. Under the reaction condition, bulk PdO was formed with an increase in the surface area by a factor of approximately two estimated by both STM image analysis and ¹⁸O isotope exchange. The oxide phase did not grow epitaxially with the metal substrate. The consequence was the formation of amorphous palladium oxide, which presented similar “cauliflower-like” structures, composed of semi-spherical oxide agglomerates around 4 nm in size on top of
the single crystals, not correlating to the original orientations. The oxide phase was about 22-27 layers deep.

Based on the PdO surface area, the steady-state turnover rates were determined as 0.72 s\(^{-1}\) on Pd(111), 0.9 s\(^{-1}\) on Pd(100) and 0.9 s\(^{-1}\) on Pd(110) at 600 K, 160 Torr O\(_2\), 16 Torr CH\(_4\), 1 Torr H\(_2\)O and N\(_2\) balance to 800 Torr. The almost identical turnover rates on the three oxidized Pd single crystals suggested that the reaction was not structure sensitive to PdO catalysts. The turnover rates reported here were generally higher than obtained on supported catalysts.

Palladium single crystals experienced an activation period for methane combustion. The nominal turnover rate (based on the geometric surface area of palladium single crystals) in the first 5 min was only about 1/5 of the steady state rate on Pd(111), 1/8 on Pd(100) and 1/4 on Pd(110). The catalyst activation was proposed partially due to the surface area increase during further oxidation, and partially to the slow oxidation rate for palladium single crystals. Palladium metal or chemisorbed oxygen on Pd was shown not as active as the oxide phase.

Surface area changed rapidly in the early stage of the reaction and then leveled off. The change in the surface area was negligible after 10 min of the reaction.

Carbon dissolution into palladium bulk was found during methane combustion under reaction condition in excess CH\(_4\) (CH\(_4\):O\(_2\) = 10:1) but not in excess O\(_2\). Removal of the dissolved carbon was difficult and required cycles of high-pressure oxygen exposure, for example 1 Torr at 780 K, followed by flashing at high temperature up to 1000 K. This carbon dissolution study provided as evidence that the kinetic behavior observed in excess O\(_2\) was not erased by carbon deposition.
In conclusion, because of using large single crystal model catalysts, the surface area can be measured precisely, the purity of the surface can be controlled, and there is no support to introduce a metal-support interaction, benchmark turnover rate of 0.9 s\(^{-1}\) is measured for the complete oxidation of methane on palladium oxide catalysts. The fact that the reaction is structure insensitive to the oxide catalysts implies that industrial catalysts should be prepared to maximize the Pd surface area without consideration of the cluster shape.
REFERENCES


Table 8.1  Surface area increase on Pd single crystals and Pd foil after CH$_4$ combustion in lean condition, 16 Torr CH$_4$, 160 Torr O$_2$, 624 Torr N$_2$, determined by STM image analysis (STM) and $^{18}$O isotope exchange ($^{18}$O).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Area Increase*</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>STM</td>
<td>$^{18}$O</td>
</tr>
<tr>
<td>Pd(111)</td>
<td>3.2</td>
<td>3.0</td>
</tr>
<tr>
<td>Pd(100)</td>
<td>2.2</td>
<td>2.0</td>
</tr>
<tr>
<td>Pd(110)</td>
<td>1.6</td>
<td>1.8</td>
</tr>
<tr>
<td>Pd foil</td>
<td>-</td>
<td>2.2**</td>
</tr>
</tbody>
</table>

* Surface area increase = \( \frac{\text{Oxide surface area}}{\text{Metal surface area}} \)

** Monteiro et al. [35]
Table 8.2  Turnover rates on Pd single crystals

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Turnover rate (s(^{-1}))*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(111)</td>
<td>0.72</td>
</tr>
<tr>
<td>Pd(100)</td>
<td>0.9</td>
</tr>
<tr>
<td>Pd(110)</td>
<td>0.9</td>
</tr>
</tbody>
</table>

* corrected to 600 K, 160 Torr O\(_2\), 16 Torr CH\(_4\) and 1 Torr H\(_2\)O
Table 8.3  Summary of turnover rates from literatures

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Agglomerate Size (nm)</th>
<th>Turnover rate $^a$ (s$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd black</td>
<td>10</td>
<td>0.5$^b$</td>
<td>[35]</td>
</tr>
<tr>
<td>Pd/Si–Al$_2$O$_3$</td>
<td>2.6-6.2</td>
<td>0.1$^c$</td>
<td>[12]</td>
</tr>
<tr>
<td>Pd/Al$_2$O$_3$</td>
<td>49-134</td>
<td>0.07-0.16$^c$</td>
<td>[12]</td>
</tr>
<tr>
<td>Pd/ZrO$_2$</td>
<td>4.3-81</td>
<td>0.1-0.7$^c$</td>
<td>[12]</td>
</tr>
<tr>
<td>Pd/ZrO$_2$</td>
<td>3-9</td>
<td>0.5-3.0$^c$</td>
<td>[60]</td>
</tr>
<tr>
<td>Pd/ZrO$_2$</td>
<td>5.5-12.5</td>
<td>0.3$^c$</td>
<td>[14, 15]</td>
</tr>
</tbody>
</table>

$^a$ TOR calculated at 600 K, 16 Torr CH$_4$, 1 Torr H$_2$O. Reaction orders were assumed to be 1 for CH$_4$, 0 for O$_2$ and –1 for H$_2$O.

$^b$ Number of sites measured from BET surface area (47 m$^2$g$^{-1}$)

$^c$ For plug flow reactor, partial pressures for reactants and products are the average of values of inlet and exit concentration
Table 8.4  Oxygen uptake and surface area increase on Pd(110) after different CH$_4$ combustion duration in lean condition, 16 Torr CH$_4$, 160 Torr O$_2$ and 624 Torr N$_2$, surface area was determined by STM image analysis

<table>
<thead>
<tr>
<th>Reaction Time (min)</th>
<th>Oxygen uptake (ML)</th>
<th>Surface Area Increase*</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>17</td>
<td>1.5</td>
</tr>
<tr>
<td>60</td>
<td>27</td>
<td>1.6</td>
</tr>
</tbody>
</table>

* Surface area increase = \( \frac{\text{Oxide surface area}}{\text{Metal surface area}} \)
Figure 8.1  STM images on Pd single crystals after CH$_4$ combustion in 16 Torr CH$_4$, 160 Torr O$_2$ and 624 Torr N$_2$, at 600 K for 60 min (a) Pd(111) (b) Pd(100) (c) Pd(110). The sample bias is 0.7 V, the tunnelling current is 0.5 nA.
Figure 8.2  Number of turnovers (CH$_4$ molecules converted per surface Pd atom) as function of reaction time on Pd(111) and Pd(100). Reaction at 600 K, 16 Torr CH$_4$, 160 Torr O$_2$, and N$_2$ balance to 800 Torr.
Figure 8.3  STM images on Pd(110) oxidized in 150 Torr O$_2$, at 600 K for 1 min. The sample bias is 0.5 V, the tunnelling current is 0.3 nA.
**Figure 8.4** Number of turnovers (CH$_4$ molecules converted per surface Pd atom) as function of reaction time on Pd(100) and on preoxidized Pd(100).

Reaction at 600 K, 16 Torr CH$_4$, 160 Torr O$_2$ and N$_2$ balance to 800 Torr. Pre-oxidation in 160 Torr O$_2$, at 600 K for 60 min.
(c)

(d)
Figure 8.5 Temperature programmed desorption spectra on Pd(100) obtained after (a) CH₄ combustion under standard lean condition, 600 K, 60 min, 16 Torr CH₄, 160 Torr O₂ and N₂ balance to 800 Torr (b) oxidation in 160 Torr O₂, at 600 K for 60 min (c) ¹³CH₄ combustion under standard lean condition, 600 K, 60 min, 16 Torr ¹³CH₄, 160 Torr O₂ and N₂ balance to 800 Torr (d) CH₄ combustion under standard rich condition, 600 K, 60 min, 160 Torr CH₄, 16 Torr O₂ and N₂ balance to 800 Torr
Chapter

9 Conclusion
We have studied in this research the oxidation of Pd single crystals: Pd(111), Pd(100) and Pd(110) in 1-150 Torr O₂ at 600-900 K for 1-180 min, and the catalytic CH₄ combustion over Pd single crystals at 160 Torr O₂, 16 Torr CH₄, N₂ balance to 800 Torr and 600 K for 60 min. To conclude the research, we found:

1. The Pd(100) and Pd(110) surfaces are more reactive towards O₂ than the Pd(111) surface by O₂ dosing in high vacuum conditions.

2. The oxidation of Pd single crystals proceeds through a three-step mechanism: (i) O₂ dissociatively adsorbs on Pd surface; (ii) atomic oxygen diffuses through a thin surface oxide layer into Pd metal; (iii) bulk PdO forms when a critical oxygen concentration was reached in the near surface region (schematically shown in Figure 9.1).

3. Five types of oxygen species are formed after exposing the Pd single crystals to O₂ depending on the Pd-O interaction: (i) surface chemisorbed oxygen; (ii) surface oxide; (iii) oxygen species in the Pd near surface region or PdOₓ; (iv) oxygen species in the Pd bulk region; (v) stoichiometric PdO.

4. The diffusion of oxygen into the near surface region depends on the Pd surface crystallography, with the highest diffusion rate on the open Pd(110). The diffusion rate follows the Mott-Cabrera parabolic diffusion law.

5. Once bulk PdO is formed, the rate-determining step for palladium oxidation is diffusion of oxygen through the bulk PdO layers. The diffusion rate also follows the Mott-Cabrera parabolic diffusion law.
6. The oxygen uptake amount on Pd single crystals increases with the population of the bulk oxygen species, which is achieved by high oxygen exposure at elevated temperatures.

7. The surface morphology of Pd single crystals during O₂ oxidation depends on the O₂ pressure, the treatment temperature and the O₂ exposure time (schematically shown in Figure 9.2).

8. Palladium oxide does not grow epitaxially on Pd single crystals after O₂ oxidation or CH₄ combustion. The oxidized single crystal surfaces form amorphous “cauliflower-like” superstructures composed of semi-spherical agglomerates 2-4 nm in size.

9. The surface area increases after subjecting the Pd single crystals to O₂ oxidation and CH₄ combustion. The highest area increase is found on the close packed Pd(111) surface. Surface area decreases after H₂ reduction of pre-oxidized Pd single crystals. To measure the surface area, we have used two techniques: O¹⁸ isotopic exchange and STM image analysis. These two approaches agree within ±20%.

10. Hysteresis in Pd oxidation rate and catalytic CH₄ combustion rate is an intrinsic feature of palladium metal, not solely due to support effect.

11. The benchmark turnover rate for catalytic CH₄ combustion is in the range of 0.72-0.9 s⁻¹ on the (111), (100) and (110) surfaces at 160 Torr O₂, 16 Torr CH₄, 1 Torr H₂O and 600 K. Therefore, methane combustion is structure insensitive over the oxidized Pd single crystal catalysts.
12. PdO is more active for CH$_4$ combustion than Pd metal or chemisorbed oxygen on Pd. The catalyst activation found during the initial 5 min for CH$_4$ combustion on Pd single crystals is partially due to the slow oxidation of Pd single crystals and partially due to the surface area changing during the reaction.

13. Carbon dissolves into Pd bulk during CH$_4$ combustion under reaction condition in excess methane (CH$_4$:O$_2$ = 10:1) but not in excess oxygen (CH$_4$:O$_2$ = 1:10).
Figure 9.1  Schematic for step for Pd single crystal oxidation
Figure 9.2  Schematic for the effects of oxygen pressure (P) and oxidation time (t) on the surface area increase on Pd single crystal after O₂ oxidation. For the pressure effect, the oxidation condition was 10 min, at 600 K; for the oxidation time effect, the oxidation condition was 10 Torr O₂, at 600 K.

\[ S_A = \frac{\text{Surface area increase}}{\text{Metal surface area}} = \frac{\text{Oxide surface area}}{\text{Metal surface area}} \]
Chapter

10 Future Work
10.1 Objective

Briefly, the objective of the current research is to achieve an understanding on the interaction of Pd model catalysts with high pressure O₂ at elevated temperatures using surface science instruments. The information is then applied to resolve fundamental questions remain for complete methane combustion. In the chapters above, we have reported and discussed the results on Pd single crystals: Pd(111), Pd(100) and Pd(110). The study on the model catalysts with Pd particles atop of thin oxide substrate will be proposed in this chapter. Compared to single crystal or foil, the model catalyst with particles on oxide shares more similarity with real catalysts; it is physically and chemically identical to the supported catalysts, except for the high surface area [1]. Therefore with this model catalyst, we are able to study the important effects of particle size, particle geometry as well as the metal-support interaction [2-6], which could by no means be addressed on the model catalysts of single crystals or foils. The study includes two tasks: (1) preparation of Pd-Al₂O₃-NiAl(110) model catalyst; and (2) oxidation of the Pd-Al₂O₃-NiAl(110) catalyst in O₂ and CH₄ combustion atmosphere.

10.2 Preparation of Pd-Al₂O₃-NiAl(110) model catalyst

The properties of the Pd-Al₂O₃-NiAl(110) model catalyst such as the surface Pd atom coverage, the geometry and the size distribution of Pd clusters, the cluster surface structures typically within atomic scales are solely determined by the deposition parameters for example, Al₂O₃-NiAl(110) substrate temperature, Pd atom deposition rate and the defects density on NiAl(110). Therefore, the correlation should be established. Another issue needs to be addressed is the thermo-stability of the Pd clusters at elevated
substrate temperatures around 600 K, the CH$_4$ oxidation temperature. It has been suggested that higher temperatures might induce the dissolution of Pd clusters into the oxide bulk [1] or the coalescence into uniformly distributed large particles [7].

10.2.1 Preparation procedure

The development of the supported model catalyst requires two steps [6]. First is to prepare a thin oxide film on a metal support. This oxide film should exhibit a well-ordered geometric structure that is identical or close to the properties of the bulk oxide [8]. In addition, it should be highly reproducible with defined geometric structure, defected structure and adsorption properties [9, 10]. The second step is the deposition of metal particles, which includes controlled nucleation and growth. The geometric structure and electronic property of the metal particles should also be well reproducible [11, 12].

10.2.1.1 Preparation of the oxide substrate

Traditional method to prepare the oxide film is oxidation of the native metals [1]. However due to large lattice mismatch, this often results in the formation of an amorphous or polycrystalline overlayer. Other methods have been proposed include evaporation of a metal onto a host crystal in an ambient oxygen atmosphere [13, 14] and oxidation of a suitable alloy that contains the metal to be oxidized. In this research we propose the oxidation of single crystal NiAl(110) to form an Al$_2$O$_3$ thin film. This alumina overlayer is exceptionally well ordered and uniform and can be reproducibly grown subjecting to slightly different preparation conditions [10, 15].
NiAl has a body centered cubic structure [16]. Clean NiAl(110) can be distinguished between the Auger transitions Ni M$_{23}$VV at 60 eV and Al L$_{23}$VV at 65 eV with an amplitude ratio of 0.77 [16]. Oxygen adsorption on NiAl(110) could result in two phases: the surface oxygen chemisorbed phase on the top Al atoms is formed by exposing NiAl(110) surface to 15 L O$_2$ at 300 K [16]; and the structural disordered phase having bulk-like oxide properties is induced after about 90 L O$_2$ exposure at room temperature [16]. Upon dosing 1200 L O$_2$ at 550 K and subsequent annealing to 1200 K, a well-defined long-range ordered Al$_2$O$_3$ structure is formed, which has a quite complex Low Energy Electron Diffraction (LEED) pattern [10]. As determined from the LEED pattern, the unit cell of the oxide film ($a = 1.055$ nm, $b = 1.788$nm, $\alpha = 88.7^\circ$) is much larger than that of the substrate and the cell is rotated 24° with respect to the substrate cell [10]. The stoichiometry and the structure of the oxide overlayer is most likely compatible with $\gamma$-Al$_2$O$_3$ [11]. Electron Energy Loss Spectroscopy (EELS), X-ray Photo-electron Spectroscopy (XPS) and Angle-resolved Ultra-violet Photoelectron Spectroscopy (ARUPS) studies indicate that this crystalline Al$_2$O$_3$ thin film consist of two aluminum layers and two quasi-hexagonal oxygen layers with oxygen surface termination [10]. Ni atoms in the bulk remain unaffected during the oxidation process [10]. Defects present on the Al$_2$O$_3$–NiAl(110) film are preferential nucleation sites for Pd deposition. These defects include oxide step edges, domain boundaries, separated oxide areas and point defects [3, 8].
10.2.1.2 Deposition of Pd clusters

After characterization of the Al$_2$O$_3$/NiAl(110) thin film, deposition of metal clusters such as Rh, Pd, Pt, Co, Ta, Ag and V have been studied with LEED, Scanning Tunneling Microscopy (STM), Transmission Electron Microscopy (TEM) and other surface sensitive instruments [12]. Two methods of evaporating metal atoms have been widely used: (1) evaporating by resistively heating a thin metal wire wound around a tungsten filament; (2) evaporating from a metal rod based on electron bombardment. During the deposition, the crystal is commonly biased with a retarding voltage in order to prevent ions from being accelerated toward the sample to create point defect. The evaporator flux is measured by a quartz microbalance [17].

For the deposition of Pd clusters, Freund group has performed a series of experiments and shown the correlation between the deposition conditions (such as substrate temperature and Pd source evaporation rate) and the Pd clusters properties [5, 6]. The nucleation and growth process of Pd clusters changed with the substrate temperature. Due to kinetic limitations, only small and disordered particles with very high cluster density and very low coverage were obtained after deposition at 90 K. Nuclei in this case were mainly heterogeneously created on point defects, coalescence among the nuclei started at an early stage accompanied by a steady decrease of the cluster density. In contrast, at 300 K, following the Volmer-Weber growth mode, much larger Pd clusters grew with flat tops, regular triangular or hexagonal in shape and reached a significantly higher coverage. The particles epitaxially grew on Al$_2$O$_3$ substrate in (111) orientation, preferentially exposing (111) facets with only small fraction (100) facets on the side of the particles. In this case, step edges and domain boundaries were still the most
prominent nucleation sites, but well-ordered clusters were rarely found there. A reduction of the lattice constant with decreasing particle size has been observed. The highest reduction was approximately 5% for clusters with a diameter of about 1.2 nm.

10.2.2 Preliminary results on Preparation of Pd-Al₂O₃-NiAl(110) model catalyst

A LEED pattern of the Clean NiAl(110) surface was shown in Figure 10.1. NiAl has an ordered body-centered cubic structure \( (a = 2.88 \text{ Å}) \). In the Auger spectrum corresponding to clean NiAl(110) (Figure 10.2(a)), we could distinguish the amplitude ratio between the Auger transition Ni M\(_{23}\)VV at 60 eV and Al L\(_{23}\)VV at 65 eV to be around 0.7. A thin layer of Al₂O₃ was prepared on top of the NiAl(110) surface by dosing \( \sim 1200 \text{ L O}_2 \) with the sample temperature held at 550 K followed by annealing at 1200 K for 10 min. A well-defined, long-range ordered Al₂O₃ structure was formed and exhibited a complicated LEED pattern as shown in Figure 10.3. Figure 10.2(b) represented the Auger spectrum obtained after the oxide formation, where the characteristic Al₂O₃ Auger transitions at 39 eV, 47 eV and 55 eV could be detected in addition to the metallic 65 eV Al peak and O KVV peak at 510 eV. Ni LVV peaks at 845 eV remained unaffected.

Palladium clusters were deposited on the thin oxide film surface when keeping the substrate temperature at 300 K with constant deposition rate \( \sim 0.1 \text{ nm min}^{-1} \). The amount of deposited palladium examined by AES vs. the nominal thickness for Pd clusters monitored with a quartz microbalance is plotted in Figure 10.4. Here Pd surface atomic concentration was obtained as the ratio between the intensity of Pd AES transition at 330 eV and the sum of the intensities of AES transitions for Al₂O₃ at 55 eV, O at 510 eV and
Pd at 330 eV. A large attenuation was detected at a coverage of $1.9 \times 10^{15}$ Pd cm$^2$ corresponding to a transition from two-dimensional to three-dimensional growth (0.1 nm thickness = $4.7 \times 10^{14}$ atoms, assuming unity sticking coefficient, which was reasonable at room temperature, the Pd atom surface density is the average of the three lowest index planes: Pd(111), Pd(100) and Pd(110)).

In Figure 10.5 typical STM images of the Pd clusters deposited on Al$_2$O$_3$-NiAl(110) substrate is displayed with the nominal thickness of 1 nm. Neither LEED nor STM have shown any indications for the formation of well-ordered facets. Pd clusters formed three-dimensional islands, which uniformly distributed on the surface (Figure 10.5(a)). The density amounted to roughly $5 \times 10^{12}$ islands cm$^{-2}$. It could then be estimated that the Pd island contained averagely around 1000 atoms, corresponding to an average particle size of approximately 3.5 nm. It was noted that the Pd particles appeared larger in the STM images (around 6-9 nm) than the above value possibly due to the convolution of the tip shape. The smaller island size and the higher island density in comparison with previous studies [5, 6] were possibly due to higher deposition rate and not homogeneously formed oxide layers. In addition, the dense distribution of Pd clusters agreed well with the AES results that a Pd film was grown under this condition.

### 10.3 Oxidation of Pd-Al$_2$O$_3$-NiAl(110) model catalyst

We propose to study the oxidation of Pd-Al$_2$O$_3$-NiAl(110) model catalyst in high pressure O$_2$ (1-150 Torr) and CH$_4$ oxidation atmosphere using surface instruments such as STM, LEED, Auger-electron Spectroscopy (AES) and Temperature Programmed Desorption (TPD). The oxidation results will be compared with that of single crystals.
The existence of bulk oxygen species and its effect on the formation of PdO will be investigated as well. Below is a short summary of the literature.

**10.3.1 Adsorption of oxygen on Pd-Al₂O₃-NiAl(110)**

The adsorption of oxygen on the Pd clusters has been shown to start from the facet edges, led to the formation of a (2×2) overlayer [4], just as in the case of oxygen adsorption on Pd(111) [18, 19]. No overall changes in the surface morphology or host lattice distortions on the top of near perfect facet of the clusters were found [18, 19]. It was then suggested that oxygen was incorporated through kink sites mostly on the unordered and/or smaller Pd clusters [4]. In comparison, NO adsorption was found to form a c(4×2) overlayer on the top facet of the clusters [4]. The dissociative adsorption of NO on cluster edges resulted in the irregular protrusions [4].

**10.3.2 Catalytic oxidation of CO on Pd-Al₂O₃-NiAl(110)**

Studies on CO catalytic oxidation on the Pd-Al₂O₃-NiAl(110) model catalyst indicated that the reaction was size and geometry dependent [2, 5, 6]. A reduced CO oxidation rate was observed for small and less-ordered particles. This behavior was related to the oxygen bulk diffusion, which as suggested by Meusel et al. [5] depended on the defect density. It has been shown that small Pd particles, exposing a high density of defect sites, could rapidly incorporate a large amount of bulk oxygen species [21]. Lattice distortion due to the interaction between metal particles and oxide support was also considered to facilitate the oxygen bulk diffusion typically on small particles [5, 6]. This oxygen species, being not susceptible to the CO oxidation reaction at low temperature, reduced
the CO sticking probability and therefore, accounted for the reduced reactivity towards CO [5, 6].
REFERENCES


Figure 10.1  LEED pattern on clean NiAl(110) surface (51 eV)
Figure 10.2  Auger-electron spectra obtained on (a) clean NiAl(110)  (b) Al₂O₃-NiAl(110)
Figure 10.3  LEED pattern on an Al₂O₃-NiAl(110) surface (51 eV)
Figure 10.4  Pd surface concentration vs. nominal deposition thickness
Figure 10.5  STM images of Pd clusters deposited on Al₂O₃-NiAl(110) surface at 300 K with the nominal deposition rate 0.1 nm min⁻¹
11 Acknowledgement
I would like to express my gratitude to the people and organizations that have supported my Ph.D. study at Worcester Polytechnic Institute.

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