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Catalytic combustion of methane on palladium single crystals

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Abstract

Catalytic methane combustion was studied over the palladium single crystals Pd(1 1 1), Pd(1 0 0) and Pd(1 1 0). Under lean reaction conditions at 600 K (O_2:CH_4 = 10:1), stoichiometric palladium oxide was formed with an increase in surface area by a factor of approximately two. The oxide phase formed a ''cauliflower-like'' surface structure composed of approximately 4 nm sized semispherical oxide agglomerates. This oxide structure was independent of the original metal single crystal orientation. The turnover rates over the oxide structure starting with metal single crystals were 0.7 s^{-1} on Pd(1 1 1), 0.9 s^{-1} on Pd(1 0 0) and 0.9 s^{-1} on Pd(1 1 0) at 600 K, 160 Torr O_2, 16 Torr CH_4, 1 Torr H_2O and N_2 balance to 800 Torr, suggesting that the methane combustion reaction is independent of the initial structure of the catalyst. Methane combustion on palladium single crystals experienced an activation period in which the initial turnover rates based on the initial Pd surface area were about 1/8–1/4 of the steady-state rates determined based on the oxide surface area. This activation period was caused by the slow oxidation of palladium single crystals and concomitant surface area increase during reaction. The increase in surface area happened mostly in the first 10 min of reaction. Carbon dissolution into the crystal was not found during methane combustion under reaction conditions in excess oxygen.

Keywords: Palladium; Palladium oxide; Oxidation of palladium; Single crystal surfaces; Methane combustion

1. Introduction

Methane is the 'greener' of fossil fuels as it has the highest hydrogen to carbon ratio of all hydrocarbons and thus produces the highest amount of energy per CO_2 formed when it is burned. Combustion of methane can be achieved through conventional flame combustion or via catalytic reaction on a catalyst surface. As compared with flame combustion, catalytic combustion is advantageous because it can be used to lower the emission level of NO_x.

Palladium has the highest turnover rate (TOR) for catalytic methane combustion [1]. One question of practical and scientific interest regarding methane combustion on Pd-based catalysts is the structure sensitivity for this reaction. In other words, does the TOR for methane combustion change as the structure of the catalyst is changed? The structure sensitivity of methane combustion on palladium does not have unanimous agreement. Hicks et al. [2,3] 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 is however different from those reported by Carstens et al. [4] and Burch and Urbano [5] who found that chemisorbed oxygen on Pd was either inactive or not as active as fully oxidized palladium for methane combustion. Garbowski et al. [6] proposed that the reaction was structure sensitive since a higher activation energy was found on less packed planes like Pd(1 1 0) and Pd(1 0 0) than on the more packed Pd(1 1 1). In contrast, Baldwin and Burch [7,8] found that the TOR changed two orders of magnitude on a series of Pd/Al_2O_3 catalysts with no correlation between particle size and TOR. Cullis and Willatt [9] did not observe strong effects of crystallite size on reaction turnover rate. Ribeiro et al. [10] found that for catalysts with different supports and prepared with different metal precursors, the rates were the same in the range of 2–10 nm. Most recently, Fujimoto et al. [11] working on Pd/ZrO_2 and Müller et al. [12,13] with Pd–Zr alloys found a ''weak'' structure sensitivity as agglomerate sizes were varied.

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The turnover rate increased by a factor of 6 [11] while increasing Pd crystallite size from 3 to 9 nm [11] and by a factor of 7 from 6 to 12 nm [12,13]. A support effect was suggested by Ciuparu et al. [14–16] who found that the turnover rate was higher on Pd/ZrO_2 catalyst than that on Pd/Al_2O_3 catalyst with the same Pd loading. These different interpretations are reflected on the variation of the reported turnover rates, at the same reaction conditions, spanning a range of three orders of magnitude [11]. The reason for this variation include support–catalyst interactions [12], catalyst activation and deactivation by impurities [8], catalyst oxidation states [2,3], and the spreading of the oxide phase over the support during reaction [17,18]. In addition, it is difficult to measure the catalyst surface area on oxides, so the TOR reported are referred to the metal, not the oxide area.

In this study, we proposed to address the structure sensitivity issue by employing palladium single crystal model catalysts. Compared with supported catalysts, single crystal catalysts have 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 [19–21]. This single crystal method has been successfully used to show the structure sensitivity for ammonia synthesis over iron catalysts and rhenium catalysts [22,23].

Methane combustion over supported palladium catalysts often shows an activation period before a steady state reaction rate is reached. In the literature, this behavior has been suggested to be due to the presence of impurities [24,25], the interaction with supports [8], the transformation between different sample oxidation states [2,3], or the morphology change of Pd crystallites [7,8]. In this study, the catalyst activation period was addressed without the effect of support on non-supported Pd model catalysts.

It is suggested that carbon diffuses in palladium bulk after an exposure to carbon sources and might affect the activity of palladium catalysts [26,27]. The dissolved carbon forms a Pd–C solid solution also referred as PdC_x phase. The content of carbon could be as high as 13–15% after exposure of palladium to a carbon atmosphere [28,29]. The dissolved carbon occupies metal octahedral sites [26,29] 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 amounts of carbon on Pd(1 1 0) surface could cause an outward expansion of the inter-planar spacing by about 4% for the first three to four surface layers [31]. The presence of carbon both on the palladium surface and in the bulk has effects on the catalyst activity. Ellipsometric studies by König et al. [32] and Graham et al. [33] reported the growth of highly porous PdO layers upon methane combustion under rich conditions (CH_4:O_2 = 1.5:1) compared with dense layers formed under lean conditions (CH_4:O_2 = 1:4). The recovery of the clean palladium phase from carbon contaminations is suggested to be achieved by heating it in an inert atmosphere at 870 K or in vacuum at 600 K [29,30], in a reduced atmosphere for example H_2 at 420 K [29,34], or in oxidizing atmosphere (O_2) at 420 K [26,29]. Carbon is also found to dissolve into palladium during catalytic methane combustion on a Pd polycrystalline foil under fuel rich conditions (CH_4:O_2 = 10:1) [35]. After the treatment, the Pd foil had a surface area increase of 18-fold compared to the two-fold increase under lean condition (CH_4:O_2 = 1:10) [35,36]. In the present work, labeled methane ($^{13}CH_4$) was used as a reactant to trace the amount of carbon dissolved on the bulk under reaction conditions. All of the ^{13}C containing species including ^{13}CO and $^{13}CO_2$ were traced to avoid the interference from ^{12}C containing impurities originally present in the reaction system. Another objective of this study was to check whether the catalyst structure sensitivity effect was erased by carbon incorporation into the bulk.

2. Experimental methods

The experiments were carried out in an especially 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 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 CH_4 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(1 1 1) (0.8 mm thick × 7.2 mm diameter), Pd(1 0 0) and Pd(1 1 0) (both 1 mm thick × 8.5 mm diameter) all made by Princeton Scientific Corp. with mis-alignment $<0.5^\circ$, 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 = 1.53×10^{15} atoms cm^{-2} on Pd(1 1 1), 1.32×10^{15} atoms cm^{-2} on Pd(1 0 0) and 0.94×10^{15} atoms cm^{-2} on Pd(1 1 0)) by comparing to standard calibration values [37–39].

Scanning tunneling microscopy images were obtained using Pt–Ir tips electrochemically etched in $NaCl/NaNO_3$ melt at around 400–450 °C. The surface area of PdO was calculated by taking discrete image pixels and joining them by a series of 3D oriented triangles. The total area was calculated by integration of the area of all individual triangles [20].

The crystal cleaning procedures consisted of cycles of Ar^+ sputtering at room and elevated temperatures, annealing in UHV, exposure to O_2 and NO_2 followed by flashing at 1000 K for Pd(1 0 0) and Pd(1 1 0) and 1100 K for Pd(1 1 1) for 60 s in

UHV. The sample cleanliness was checked by TPD, AES and LEED.

The methane combustion reaction on Pd single crystals was performed in the high-pressure reaction cell (615 cm^3 in volume) in a batch mode. The reaction gases were introduced from a gas manifold in the following order: N_2 (624 Torr), O_2 (160 Torr), and CH_4 (16 Torr). For labeled methane ($^{13}CH_4$) experiments, $^{13}CH_4$ was used. 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 cm^3 min^{-1}. This circulation was continued throughout the reaction to effectively eliminate external mass transfer limitations [36]. Reaction was normally carried out at 600 K for 60 min with about 2.5% of the CH_4 being converted. 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 ^{18}O isotope exchange experiment to measure the surface area change on Pd single crystals after CH_4 combustion was performed in a high-pressure reaction cell similar to the one described above and following the procedure described before [36]. Briefly, an oxidized palladium sample was exposed to 5 Torr $^{18}O_2$ at 600 K for 12 s, and the uptake of ^{18}O exchanged was then measured by TPD by analyzing all gases containing labeled oxygen.

3. Results

3.1. Characterization of Pd single crystals before and after reaction

The state of the Pd single crystal surface was examined by LEED, AES, TPD and STM before and after catalytic methane combustion reactions. Before reaction, only features corresponding to metallic Pd could be observed. LEED revealed a clear single crystal structure with sharp diffraction spots. STM showed a smooth surface with terraces separated by monoatomic steps. After reaction, no metal Pd single crystal LEED pattern was observed. 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_2 [36,40]. The oxygen uptakes on the Pd(1 1 1), Pd(1 0 0) and Pd(1 1 0) surfaces determined by TPD were 22, 24 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(1 1 1), Pd(1 0 0) and Pd(1 1 0) after the methane combustion treatment in excess O_2 have been presented elsewhere [41]. They showed a similar PdO surface morphology on the three single crystals, not correlated to the original orientation of the single crystal metal. No X-ray diffraction pattern corresponding to PdO could be observed; only the peaks corresponding to the metal were observable. 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 Pd single crystal surface area increase after methane combustion under standard lean condition was determined by STM image analysis and ^{18}O isotope exchange. Table 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 [36] which is listed in the last row in Table 1.

Table 1
Surface area increase on Pd single crystals and Pd foil after CH_4 combustion in lean conditions, 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)

Sample	Surface area increase[a]		References
	STM	^{18}O	
Pd(1 1 1)	3.2	2.6	[41,45]
Pd(1 0 0)	2.2	2.0	[41,45]
Pd(1 1 0)	1.6	1.9	[41,45]
Pd foil	–	2.2	[35]

[a] Surface area increase = oxide surface area/metal surface area.

3.2. 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 reaction conditions [42–44]. Before measurement of the reaction kinetics, a blank experiment was performed to test the background activity of the reaction cell. A stainless steel foil with the same size as the Pd single crystals was mounted on a standard sample holder and exposed to the standard lean methane combustion atmosphere at 600 K for 60 min. No CO_2 signal could be detected (by gas chromatography) showing a negligible background contribution.

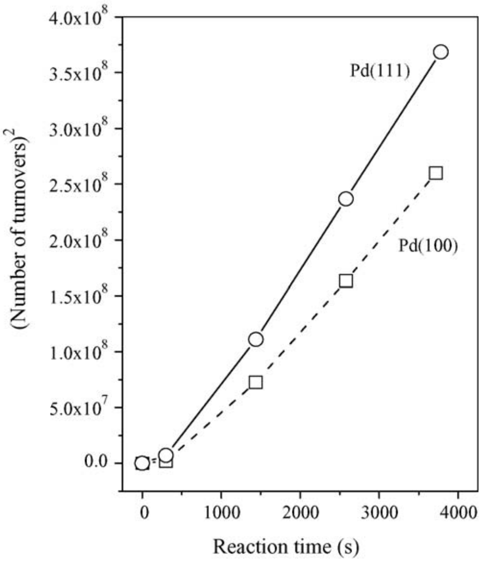

Fig. 1. Number of turnovers (CH_4 molecules converted per surface Pd atom) as a function of reaction time on Pd(1 1 1) and Pd(1 0 0). Reaction at 600 K, 16 Torr CH_4, 160 Torr O_2, and N_2 balance to 800 Torr.

The turnover rate on the three Pd single crystals was defined as the number of methane molecules converted per unit of time per Pd atom on the surface. As we explained before [36,45,46], for a batch reactor if we assume the reaction order for 1 for CH_4, −1 for H_2O (reaction is inhibited by water), and 0 for both O_2 and CO_2, the square of the methane conversion varies linearly with the reaction time (t) in the limit of low methane conversion. If follows then that the number of CH_4 molecules converted per Pd atom on the surface (number of turnovers, N) will be proportional to the conversion. Thus, the reaction rate is obtained by calculating the slope of the line in the N^2 versus t plot. A typical plot for Pd(1 1 1) and Pd(1 0 0) is shown in Fig. 1. It is noted that the single crystal catalyst was not fully activated at the early stages of reaction. An activation period was observable in the first 5 min (Fig. 1). 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 1), the turnover rates for catalytic methane combustion over Pd single crystals are 0.7 s^{-1} on Pd(1 1 1), 0.9 s^{-1} on Pd(1 0 0) and 0.9 s^{-1} on Pd(1 1 0) at 600 K, 160 Torr O_2, 16 Torr CH_4 and 1 Torr H_2O. The turnover rates obtained on Pd single crystals, foils, supported catalysts and palladium black mostly in the critical range of 1–10 nm [10–13,36] were summarized and tabulated in other publications [41,45]. The reported turnover rates in the literature, at the same reaction conditions, spans a range of three orders of magnitude [11]. Note that the turnover rate obtained in this research, though internally consistent, was on average two times lower than that by Zhu et al. [41,45] obtained on a similar reaction system. The single crystal surface structure was retrievable by carrying a temperature programmed desorption up to 1100 K for Pd(1 1 1) and 1000 K for both Pd(1 1 0) and Pd(1 0 0). Clear Pd single crystal (1 × 1) LEED patterns with sharp integral spots were observed after the high temperature cleaning.

3.3. Catalyst activation

Palladium single crystal experienced an activation period during methane combustion as shown in Fig. 1. The initial turnover rate, assuming a constant slope during the first 5 min and a constant surface area equal to the initial metal one, was around 1/5 of the steady state turnover rate on Pd(1 1 1), 1/8 on Pd(1 0 0) and 1/4 on Pd(1 1 0). Experiments were performed on pre-oxidized surfaces to test the hypothesis that the active phase is the oxide. The Pd single crystals were oxidized in O_2 (1–150 Torr) at 600 K for various times [20]. It was found that a fresh single crystal would not be oxidized at the early stages of oxidation but oxygen would diffuse into the bulk [20,21]. For example, bulk oxide was not formed by exposure of a Pd(1 1 0) surface to 150 Torr O_2 at 600 K in the first minute of reaction with the surface presenting a semi-ordered structure with small agglomerates around 1.5–2 nm in diameter growing along the $\langle 1\bar{1}0\rangle$ direction (Fig. 2). In addition, LEED revealed a weak streaky Pd(1 1 0) (1 × 1) pattern. The surface area increase was estimated using STM images to be only 0.2 times higher after this treatment. Further support to the hypothesis that the active surface is the oxide came from 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(1 0 0) as shown in Fig. 3.

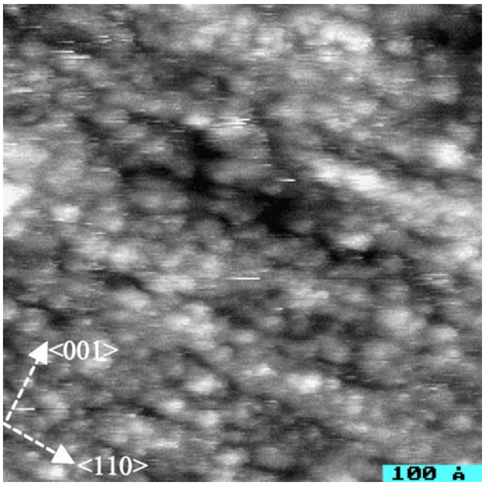

Fig. 2. STM images on Pd(1 1 0) in 150 Torr O_2, at 600 K for 1 min with sample bias of 0.5 V, and 0.3 nA tunneling current.

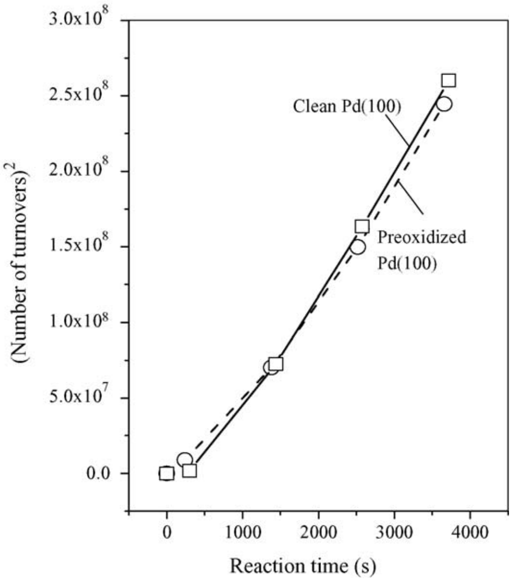

Fig. 3. Number of turnovers (CH_4 molecules converted per surface Pd atom) as a function of reaction time on Pd(1 0 0) and on preoxidized Pd(1 0 0). Reaction at 600 K, 16 Torr CH_4, 160 Torr O_2 and N_2 balance to 800 Torr. Pre-oxidation in 160 Torr O_2, at 600 K for 60 min.

Table 2 lists the oxygen uptakes and surface area increases determined on Pd(1 1 0) after methane combustion reaction times of 10 and 60 min. The amount of oxygen uptake during CH_4 combustion increased with the time of reaction, being 17 ML at 10 min and 27 ML at 60 min. The surface area increase was 1.5 and 1.6 after 10 and 60 min of reaction. Thus, the surface area reaches a stable level after 10 min of reaction.

Table 2
Oxygen uptake and surface area increase on Pd(1 1 0) after different reaction times for CH_4 combustion in lean condition, 16 Torr CH_4, 160 Torr O_2 and 624 Torr N_2

Reaction time (min)	Oxygen uptake (ML)	Surface area increase[a]
10	17	1.5
60	27	1.6

Surface area was determined by STM image analysis.

[a] Surface area increase = oxide surface area/metal surface area.

3.4. Carbon dissolution

Temperature programmed desorption of O_2 (mass 32), CO (mass 28) and CO_2 (mass 44) on a Pd(1 0 0) single crystal after methane combustion under standard lean condition is shown in Fig. 4. The O_2 desorption peaked at 780 K, consistent with the TPD obtained after oxidation of Pd(1 0 0) in 160 Torr O_2, at 600 K for 60 min as shown in Fig. 5. The amounts of oxygen uptake after CH_4 combustion reaction and Pd oxidation in O_2 were the same and corresponded to 24 ML.

Both CO and CO_2 desorption occurred at two different temperatures (Fig. 4). The lower temperature desorption peak for CO_2 was at 450 K and the higher temperature peak at 810 K. The areas of the desorption peaks were equivalent to 0.3 and 0.12 ML of CO_2 at 450 and 810 K, respectively. Similarly, the desorption of CO occurred at 580 and 810 K, with the integral areas corresponding to 0.1 and 0.05 ML CO at 580 and 810 K. The lower temperature CO and CO_2 desorption also appeared at 540 K after Pd(1 0 0) oxidation in 160 Torr O_2 (with no CH_4 present) as shown in Fig. 5. In addition, the higher temperature CO and CO_2 desorption at 760 K were observable in Fig. 5 with nominal coverage of 0.1 ML of CO_2 and 0.05 ML of CO.

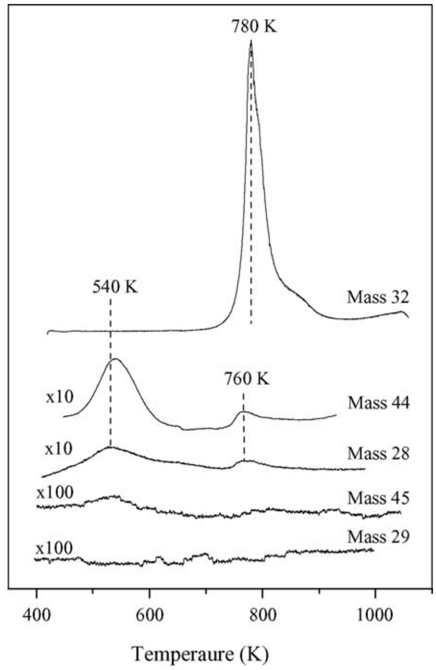

Fig. 5. Temperature programmed decomposition spectra on Pd(1 0 0) obtained after oxidation in 160 Torr O_2, at 600 K for 60 min.

To differentiate the effect of carbon impurities originally presented in Pd(1 0 0) from the influence of methane combustion, labeled methane ($^{13}CH_4$) was used as a reactant. A blank experiment was performed by monitoring the desorption of ^{13}C containing species including ^{13}CO (mass 29) and $^{13}CO_2$ (mass 45) after oxidation of Pd(1 0 0) in 160 Torr O_2 at 600 K for 60 min (no CH_4 present in the reaction mixture). No desorption was observable as shown in Fig. 5 ensuring the sample was ^{13}C-

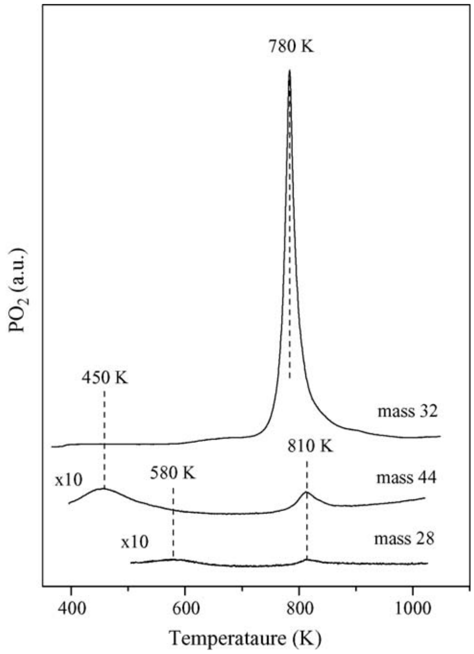

Fig. 4. Temperature programmed decomposition spectra on Pd(1 0 0) obtained after CH_4 combustion under standard lean condition, 600 K, 60 min, 16 Torr CH_4, 160 Torr O_2 and N_2 balance to 800 Torr.

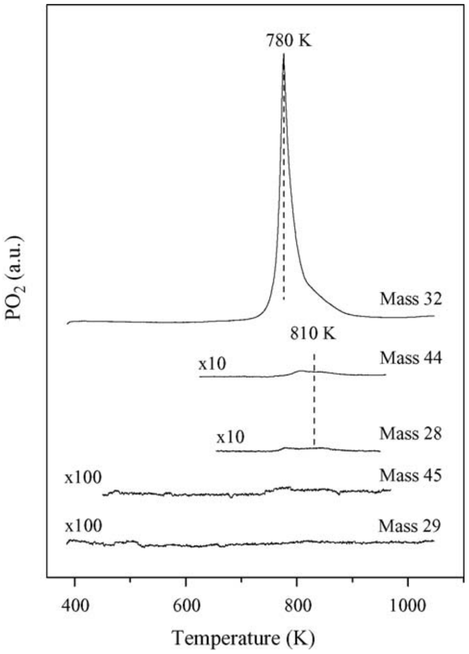

Fig. 6. Temperature programmed decomposition spectra on Pd(1 0 0) obtained after $^{13}CH_4$ combustion under standard lean condition, 600 K, 60 min, 16 Torr $^{13}CH_4$, 160 Torr O_2 and N_2 balance to 800 Torr.

free. The combustion of $^{13}CH_4$ was carried out under the standard lean conditions. The TPD result on the single crystal catalyst after reaction is shown in Fig. 6. No signal from ^{13}CO and $^{13}CO_2$ could be detected. Note that the intensities for ^{12}CO and $^{12}CO_2$ desorption peaks remained unchanged in Figs. 4–6; the area of the desorption peaks in Fig. 6 was equivalent to 0.09 ML $^{12}CO_2$ and 0.07 ML ^{12}CO at 810 K.

4. Discussion

4.1. Reaction structure sensitivity on oxide phase

To identify whether a reaction is sensitive to the structure of the catalyst, one needs 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 [47,48]; 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 [47,48]. 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 used the metallic planes Pd(1 1 1), Pd(1 0 0) and Pd(1 1 0) to simulate the most common faces on a metal crystallite and then measured 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 is an indication that the complete combustion of methane over oxidized Pd single crystals is independent of the structure of the catalyst. Indeed, under the standard catalytic reaction condition in excess O_2, stoichiometric palladium oxide was formed. The fact that we did not observe any XRD pattern of PdO, which should have been detectable for the thickness of PdO layer formed is an indication that the oxide layer is either amorphous or 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. Amorphous PdO presented similar ‘‘cauliflower-like’’ surface structures composed of semispherical oxide agglomerates around 4 nm in size. The formation of stoichiometric PdO was characterized by the complete fading of the Pd single crystal (1×1) LEED pattern and the 0.7 O/Pd atomic ratio detected by AES. It is also noted that the turnover rate on Pd single crystals was generally higher than on supported catalysts [41,45], indicating that the existence of other factors affect the rate on supported catalysts.

In contrast to the growth of amorphous PdO we found here, the TEM studies by Lyubovsky et al. [49] and the in situ Raman studies by Carstens et al. [4] suggested the formation of crystalline PdO during oxygen oxidation or catalytic methane combustion of Al_2O_3 and ZrO_2 supported Pd catalysts. The conflict with the literature results could be understood by the Raman observation by Su et al. [50] who reported that during oxidation of a Pd/Al_2O_3 supported catalyst in O_2 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. It was determined using in situ Raman that only 7% PdO was crystallized during oxidation at 533 K [50]. Even after oxidizing a Pd/Al_2O_3 catalyst at a temperature of 1043 K in 1 atm air, transmission electron microscopy studies by Datye et al. [51] 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. [6] based on the argument that PdO with tetragonal lattice structure was able to epitaxially form on top of the less packed square (1 0 0) plane and rectangle (1 1 0) plane; whereas oxidation of dense hexagonal (1 1 1) plane occurred with profound metal reorganization, thus requiring a higher activation energy [6]. This argument is possibly not complete since in order to grow an epitaxial film, a close lattice match with the substrate to minimize interfacial strain, compression or relaxation depending on the lattice parameters $a_{\mathrm{film}} <(>) a_{\mathrm{sub}}$, is required [52]. 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(1 1 1), Pd(1 0 0) or Pd(1 1 0). Even if the interfacial strain due to the lattice noncommensurability were relived, and an epitaxial oxide film was grown for the first few layers, the rapid accumulation of strain energy with the film thickness due to the inherent stiffness of the oxide would exaggerate the misfit dislocation, resulting in film buckling, the formation of 3D islands and the ultimate morphological transformation to amorphous oxide [52,53]. 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.

4.2. Catalyst activation

This research confirms that methane combustion on palladium single crystal catalysts under standard lean condition experiences an activation period. The activation was observed to occur in the first 5 min of reaction. The initial turnover rates based on the initial Pd surface area were about 1/8–1/4 of the steady-state rates determined based on the oxide surface area. The activation period has also been reported on supported Pd catalysts [2,3,7,8,24,25]. In this study, the presence of impurities on the single crystal surfaces to block catalytic active sites could be ruled out by AES, which did not detect any noticeable amount of impurities, for example SiO_2, before and after reaction. There is no catalyst-support interaction for our samples. Although the surface morphology changed during the reaction with an increase in 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 conditions (see Table 1). Therefore, catalyst activation is the consequence of the slow palladium bulk oxidation. A previous study from our group however showed no activation period for methane combustion over a Pd polycrystalline foil [36]. Since Pd metal is known to present no activity for methane combustion at low temperature [4,45,54], this different activation behavior on the two types of model catalysts could be attributed to the higher PdO formation rate on foils than on single crystals. Studies on oxidation of Pd single crystals in high pressure O_2 (1–150 Torr) suggested that the oxygen species diffusing in the palladium near surface region is likely the precursor to bulk oxidation [20,21]. The concentration of oxygen increases as the oxygen atoms diffuse into the Pd metal continuously. At a certain critical concentration, bulk oxide phase nucleates and grows [20,21]. It is expected that the oxygen diffusion from surface to bulk depends 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(1 1 1) and Pd(1 0 0) surfaces, and on a Pd(1 1 0) surface initial oxide nucleation was found along the steps in the $\langle 1\bar{1}0 \rangle$ direction [20,21]. Compared with the single crystal samples, which have step and defect density estimated to be less than 1%, Pd polycrystalline foil presents a large number of steps, kinks and defects created by grain 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 CH_4 combustion in standard lean conditions [36]. The oxygen uptakes were 60 and 85 ML at 10 and 60 min of the reaction on the Pd foil respectively [36]. In comparison, the oxygen uptakes on Pd single crystals were in the range of 22–27 ML after 60 min of the CH_4 combustion in excess O_2. The much higher oxygen uptake amount in addition to the lack of activation period on a Pd foil as compared to Pd single crystals (Table 2) is an indication that the oxidation of Pd foil is faster compared with the catalytic reaction. Thus, methane combustion occurred on a not fully oxidized Pd single crystal surface in the initial stage as suggested in Fig. 2 and no catalyst activation was observable on a fully oxidized sample as shown in Fig. 3.

The fact that a straight line was obtained after the activation period (Fig. 1) indicated that although the Pd single crystal was constantly being oxidized under reaction conditions in excess O_2, the major surface expansion due to oxidation happened in the early stages of reaction and then the surface area increase leveled off; otherwise, the reaction rate would have increased with time. The surface area increases of 1.5 and 1.6 after 10 and 60 min of CH_4 combustion as listed in Table 2 consolidated this conclusion.

It is generally believed that a monolayer of oxygen is rapidly adsorbed on the palladium surface under reaction conditions [54]. If chemisorbed oxygen were more active than the oxide phase [2,3], we would expect a higher activity in the initial stage of reaction. Instead, a lower activity was observed in this study, which further supports the conclusion by Carstens et al. [4] and Burch and Urbano [5] that chemisorbed oxygen is either inactive or not as active as oxidized palladium for CH_4 combustion.

4.3. Carbon dissolution

We have shown in this study from TPD spectra (Figs. 4–6) that there is no evidence for carbon dissolution in palladium single crystals during methane combustion under lean conditions. The carbon oxides desorbed at low temperatures 450 K and 580 K in the form of CO_2 and CO (Fig. 4) did not originate from the reaction mixture since the desorption temperature was lower than the reaction temperature of 600 K [36]. In addition, the low temperature desorption was also observed after oxidation of a Pd single crystal sample in O_2 atmosphere (with no CH_4 present) as shown in Fig. 5. They originated from impurities deposited during transfer from the reactor to the UHV chamber. The CO and CO_2 desorption at high temperature of 810 K after methane combustion (Fig. 4) was not due to CH_4 deposition either, because the desorption peaks were of the same intensities as the 760 K peaks obtained after Pd oxidation in pure O_2 (Fig. 5). The desorption of CO and CO_2 at about 750 K from Pd after oxidation in oxygen atmosphere (Fig. 5) suggested that the Pd single crystal was contaminated by dissolved carbon. This carbon impurity was present mainly in the bulk phase, so a carbon-free surface was available after cleaning cycles in the analysis chamber. However, extensive oxidation for example in high pressure O_2 at elevated temperatures for instance 600 K might segregate the carbon species closer to the surface again and they desorb as CO_2 and CO when the bulk oxide decomposes during temperature programmed desorption. The fact that no signal from ^{13}CO and $^{13}CO_2$ could be detected using $^{13}CH_4$ as reactant (Fig. 6) implied that the amount of carbon deposited on the surface during combustion reaction in excess O_2 was negligible.

Baldwin and Burch [7,8] 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. They thus hypothesized that the deposition of carbon might re-order the surface of palladium oxide [7,8]. 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 conditions in excess oxygen, see Table 1. This observation was rationalized as a major lattice expansion during oxidation [20,21]; but not due to the existence of carbon (Fig. 6). Thus, at least under lean conditions, 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 effects on the reaction kinetics is excluded.

5. Summary

The catalytic combustion of methane in excess oxygen (O_2:CH_4 = 10:1) was studied at 600 K over three palladium single crystals, Pd(1 1 1), Pd(1 0 0) and Pd(1 1 0). These crystals compose the most common faces on a metal crystallite. Under reaction conditions, stoichiometric palladium oxide was formed with an increase in the surface area by a factor of approximately two as measured by both STM image analysis and ^{18}O 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 and showing no relationship 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 $0.7\ s^{-1}$ on Pd(1 1 1), $0.9\ s^{-1}$ on Pd(1 0 0) and $0.9\ s^{-1}$ on Pd(1 1 0) at 600 K, 160 Torr O_2, 16 Torr CH_4, 1 Torr H_2O and N_2 balance to 800 Torr. The similar turnover rates on the three oxidized Pd single crystals suggest that the reaction is not sensitive to the structure of the catalyst. The turnover rates reported here were higher than the ones obtained on supported catalysts. Palladium single crystals experienced an activation period during 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(1 1 1), 1/8 on Pd(1 0 0) and 1/4 on Pd(1 1 0). The catalyst activation was proposed to be due to a combination of surface area increase during reaction and to the slow oxidation rate for palladium single crystals. Palladium metal or chemisorbed oxygen on Pd was shown previously in the literature not to be as active as the oxide phase. The surface area changed rapidly in the early stages of the reaction and then leveled off. Further changes in the surface area were negligible after 10 min of reaction. Carbon dissolution was not found during methane combustion under reaction condition in excess O_2.

In conclusion, a benchmark turnover rate was measured for the complete oxidation of methane on palladium oxide catalysts. The measurement was possible by the use of large single crystal model catalysts which allowed the surface area to be measured precisely, the purity of the surface to be controlled, and metal-support interactions to be avoided.

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