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Summary

Palladium (Pd) is an attractive catalyst for a range of new combustion applications comprising primary new technologies for future industrial energy needs, including gas turbine catalytic combustion, auto exhaust catalysts, heating and fuel cells. Most gas turbine companies are now developing some version of catalytic combustion of natural gas using Pd for advanced turbine designs, and multiple design efforts are also underway for ultra-low NOX lean burn catalytic combustors for burning natural gas, bio-derived fuels, and conventional liquid fuels in microturbines for distributive power generation and hybrid electric vehicle gas turbines. However, Pd also poses particular challenges because it changes both chemical state and morphology as a function of temperature and reactant environment and those changes result in positive and negative changes in activity. Interactions with the support, additives, water, and contaminants as well as carbon formation have also been observed to affect Pd catalyst performance.

The research performed under the DoE Grant No. DE-FG02-96ER14679 resulted in new insights regarding several key issues related to the use of palladium-based catalysts for auto exhaust applications and methane combustion. These key issues were studied both from a reaction engineering and surface science viewpoint to provide scaling information and mechanistic insights.

1. Reoxidation of metallic Pd while cooling in air from high temperature occurs through a nucleation driven mechanism. This was noted by TPR/TGA cycles with TEM/XPS observation of the catalysts at points in the cycles [1, 2]. Considerable roughening was observed to result from reoxidation. Fully oxidized samples show multiple surface planes in HR-TEM. A similar process was observed with model catalysts under high vacuum excursions observed when a catalyst is reduced and then exposed to an oxidizing reaction environment and also has implications for activation of close-coupled exhaust catalysts, where fluctuations in stoichiometry and temperatures allow oxidation and reduction cycles.

2. Confirmation of the nucleation mechanism was obtained for Pd(111) using scanning tunneling microscopy (STM) [3]. Intermediate phases present during the reoxidation process were identified. Coincident phases coexisted with long lifetimes. For Pd (111) and Pd (100), as the oxygen partial pressure is increased at constant temperature the Pd-O system passes through the following sequence of phases: 1) bulk Pd with a bare Pd surface; 2) a simple chemisorbed layer with O atoms on top of a bulk-terminated Pd surface and a heat of adsorption of ~55 kcal/mol; 3) a mixed Pd-O surface phase with a unique structure and Pd-O bond strength intermediate between chemisorbed O and bulk PdO; 4) oxygen deficient PdO characterized by heat of formation of ~25 Kcal/mol; 5) stoichiometric PdO. The intermediate phases grew preferentially as peninsulas and islands. The existence of at least one stable intermediate state was confirmed. In our studies of supported Pd catalysts using high resolution transmission electron microscopy (HRTEM) samples that were quenched
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during early phases of the reoxidation process showed patches of oxide and metal phases on individual particles while fully oxidized particles consisted of many surface planes.

3. Considerable controversy exists over possible Pd-O states that can exist and how reactivity is affected. Although much has been made in the literature about potential differences between "lattice" and "adsorbed" oxygen species, PdO surfaces expose only a single type of oxygen species: an oxygen atom bridge bound to two Pd atoms. Our studies of methane oxidation using labeled oxygen confirm that only one form of oxygen is used in the reaction [4]. The carbon oxides reflect the isotopic composition of the catalyst surface whereas the distribution of isotopically labeled oxygen in the water produced reflects the composition of the catalyst bulk. This is consistent with the observation that water is retained by the catalyst and that the hydrogen samples the bulk [4]. Both the (001) and (110) bulk-terminated surfaces expose only a single type of oxygen species, oxygen atoms bridge bound to two Pd atoms. Our results clearly indicate that, because of the lower rate of water desorption relative to the rate of isotopic equilibration between surface and bulk oxygen and because hydrogen samples the bulk, the water molecules produced in the combustion reaction reflect the composition of the bulk PdO.

4. The inhibition of reoxidation of palladium after complete reduction at high temperatures was observed for a broad range of supports [5] and was also found to occur for single crystal palladium under high vacuum conditions. The inhibition of Pd reoxidation and the corresponding activity hysteresis was observed with polycrystalline PdO supported on alumina, zirconia and several ceria-zirconia mixtures during temperature programmed methane combustion experiments. The identity of the support was shown to strongly affect the degree of hysteresis. Supports with high oxygen mobility (Pd particle size fixed) showed the least hysteresis. On cool-down, stopping the temperature decrease and maintaining the catalyst at a fixed temperature for hours resulted in a cessation of oxygen uptake (as measured by XPS), although the activity for methane combustion doubled over the same time scale. As temperature is decreased in steps a small amount of additional oxide is formed within minutes until the temperature where oxidation becomes fast. This passivation effect was noted for all systems studied, but support interactions (Pd particle size held constant) were observed to strongly influence the reoxidation temperature.

5. Catalysts were fabricated with high N₂ selectivity at high conversion of NO and CO [6]. The contact between the ceria and Pd phases was found to be critical in achieving this effect. The catalyst with the highest selectivity for N₂ also had the smallest hysteresis for methane oxidation, consistent with the ceria/Pd interface playing an important role. This result is consistent with the work of Howe and Davis reported at the 2000 DOE meeting in Rockville, MD. An electronic interaction between ceria and Pd phases was not observed; however, the presence of ceria and how it is distributed affected the oxidation state of the palladium and, thus, reactivity. Catalysts with equivalent Pd loadings and particle sizes but different distribution of ceria were found to have widely varying N₂ selectivities.

6. Due to the higher temperature operating conditions of close-coupled catalysts and the operation around the stoichiometric equivalence ratio, carbon deposition on the catalyst is possible. In our work on this project we characterized carbon deposition on Pd/ceria catalyst supported on zirconia under auto exhaust remediation conditions [6]. At high temperatures (above 725K) the disproportionation reaction CO + CO → CO₂ + C was found to be important. By surface carbon titration with oxygen pulses, quantitative measurements of the carbon deposition amounts were carried out for different reaction conditions. We are currently
using this data to determine carbon deposition kinetics. We propose to expand this work using HR TEM and XPS measurements performed on lightly pre-carbided catalyst samples. These methods will allow understanding of carbon deposition to allow development of methods to diminish or prevent carbon depositions at the catalyst surface during operation at fuel rich conditions that would be important for fuel processing reactions.

7. Oxidation of alkanes over PdO is strongly affected by water poisoning (reaction order of about -1) at temperatures below 725K in minute time-scale pulsed reaction and to significantly higher temperatures under continuous flow conditions where readsorption of water is important [5]. Oxidation studies were carried out for propane, ethane and methane. Previous studies have assumed that water adsorption/desorption is equilibrated over all conditions used in laboratory studies. We, however, have shown [7] that water effect is not equilibrated on the minute time scale until T>725K. Pulsed reaction gives significantly higher reactivity than continuous, different heating rates give different reactivity for reaction under low temperature, continuous flow conditions. The reaction order with respect to water, also changes with temperature. This can create artifacts in temperature programmed reaction (TPR) data taken at low temperatures. Running in a pulsed mode with a frequency of 1/5min results in significantly higher activity than obtained with continuous flow. At the high temperature, low oxygen conditions, however, typical of close-coupled converter, this effect is not usually important. Water poisoning is not a factor over the metallic state of the catalyst. Cycling to low temperatures and high oxygen concentrations can markedly increase the water poisoning effect because, as we have shown, water adsorption/desorption is not equilibrated.

8. Partial reduction can cause long lasting positive excursions in reactivity. This was observed both with bulk PdO and PdO supported on zirconia, alumina, and those supports with ceria added. During reoxidation of a fully reduced catalyst, methane oxidation activity begins to increase before bulk oxide is formed. On the fuel lean side, (1% Methane, 4% oxygen) hydrocarbon oxidation activity was found to be highest for a transient sub-stoichiometric oxide state. It should be noted that part of the increase in activity is due to an increase in surface area due to the roughening that occurs on reoxidation. This is not the whole story, however, as the methane oxidation rate increases and then decreases as PdO is reduced in steps with methane. In this case the surface is being continually reduced and surface area continually decreases [8]. This is supported by recent studies of Altman and co-workers showing CO oxidation rate increased when the oxygen coverage of a Pd (111) surface decreased. However, a maximum rate is reached corresponding to the highest concentration of a (2x2) adsorbed oxygen structure at the surface, a further decrease in the oxygen coverage giving lower CO oxidation rates. Also, for Pd supported on α-alumina, steady-state activity increased for lean methane – air mixtures as the catalyst was continually reduced at high temperature with a consequent decrease in PdO surface area [9].

9. At low temperatures T<700K in presence of methane the exchange of surface oxygen with the gas phase is slower than the exchange with the bulk for an unsupported PdO catalyst [4]. This is important because it implies a steady state bulk and surface oxygen deficiency. It also has implications for the long lifetime coexistence of phases as noted in point #2 above and in Appendix I. We obtained similar results for a zirconia supported catalyst, consistent with data reported by other authors [10], but also found that oxygen exchange with the zirconia support and the PdO catalyst is fast especially at T> 700K so interpretation of the data is not straightforward.
Introduction

Methane oxidation over Pd based catalysts has been extensively studied over the past fifteen years due to its attractive potential for catalytic combustion applications [e.g. 1,4,5,7-40]. Natural gas will be increasingly used as a source of energy in the future. Because the methane molecule contains four C-H bonds and only one carbon atom, combustion of methane yields the lowest amount of CO₂ (gas leading to the greenhouse effect) per unit of produced energy. With stricter regulations on CO₂ emissions to the atmosphere, this makes natural gas even more attractive as a fuel for the purposes of energy production. In addition, oil is a dwindling resource, which will probably be exhausted before the middle of the XXI century. The supply of natural gas and coal-derived methane, however, is expected to last though the foreseeable future.

Supported palladium has been found to be the most promising catalyst for the complete oxidation of methane [14]. Numerous studies of this catalytic reaction have been carried out in recent years [20-40]. However, questions remain yet open about many key aspects of the behavior of palladium catalysts under methane combustion conditions. Among these, the following issues were addressed in the research studies sponsored under the DOE grant:
1. The correlation between thermal stability of the PdO phase, the rate of Pd reoxidation on cooling down the reaction temperature, and the chemical nature of the support;
2. Surface science studies of Pd oxidation;
3. Microscopic scale morphological modifications of the palladium phase during reoxidation;
4. The contribution of PdO lattice oxygen and support oxygen to the methane combustion reaction;
5. The study of different oxygen states at the Pd surface during palladium reoxidation;
6. Characteristics of the water inhibition effect in methane combustion over PdO-based catalysts;
7. Combustion activity of partially reduced PdO catalysts – activity excursions;
8. Investigations of the synergetic effects between ceria and palladium particles;

Important features of each of these issues are discussed below. The details of the work are given in the noted papers. Submitted and in press papers are included in the Appendices noted.


Although, an impressive research effort has been invested in this topic, the mechanism by which the support influences the stability of the PdO phase and the catalytic activity is not clear. Earlier work did not address whether interactions of the palladium phase with the support influence the catalyst activity directly or simply through the effect on the oxidation – reduction behavior.

Rodriguez et al [41] investigated the interactions between palladium and zirconia support at different temperatures by means of in situ controlled atmosphere electron microscopy (CAEM). They attributed the behavior of the supported catalyst to the strong interaction between the freshly generated PdO phase and the zirconia support. Garbowsk et al. [24] observed that
during reoxidation the palladium phase experienced restructuring, but concluded that the PdO roughening does not produce catalyst activation. Narui and co-workers [42] suggested that the PdO phase is stabilized by solid–solid reaction with the zirconia support at 773 - 1173K resulting in a surface solid solution. They claimed that the amount of PdO incorporated in such a solid solution increases with the calcination temperature from 773 to 1173K. Above this temperature the amount of PdO phase was found to decrease significantly. Primavera et al [43] reported that a solid solution of ceria, zirconia and palladium oxide prepared by co-precipitation of the mixed nitrate solutions segregated to give metallic palladium particles after calcination at temperatures above 1273K. These authors showed that the segregation is not reversible as the temperature is lowered and persists at room temperature.

In this work, methane combustion tests were performed at the same reaction conditions (heating – cooling rate, contact time, and pretreatment history) with three different catalytic systems having approximately the same metal loading. Consequently, the differences in their behavior are assumed to be mainly due to their different carriers. The supported catalysts have essentially the same particle sizes with the alumina-supported slightly smaller, however the mechanical mixture (produced by mixing pure PdO from Aldrich with the zirconia powder used as support for the supported catalyst) is characterized by a broad array of larger particles, certain different features of the TPR profiles for the mechanical mixture could also be due to differences in particle size.

The important deactivation of the catalyst observed between the first and the second heating – cooling cycles is primarily caused by a loss in its catalytic surface area due to particle sintering during the high temperature exposure, as confirmed by X-ray diffraction analysis. The XRD results showed almost the same increase in the particle size for the particles supported on alumina and zirconia, suggesting no support effect in the sintering process.

Earlier investigations by Farrauto et al. [21] revealed strong but differing interactions between both PdO and metallic palladium phases, and different supports as measured by oxide decomposition and reformation temperatures determined in air-flow thermogravimetric analysis (TGA) experiments. These authors reported higher PdO decomposition temperatures for catalysts supported on alumina than for those supported on ceria or zirconia, but claimed there is no correlation between the oxygen mobility of the support and the PdO decomposition temperature. In this work, Datye also observed higher PdO decomposition temperatures in TGA experiments for unsupported and $\gamma$ Al$_2$O$_3$ supported particles than for $\alpha$ Al$_2$O$_3$, zirconia or ceria supported PdO. Rodriguez et al. [41] investigated the interactions between palladium and zirconia supports at different temperatures by means of in situ controlled atmosphere electron microscopy (CAEM). They reported a strong interaction between the PdO phase and a zirconia support and found that the strength of the interaction is temperature dependent.

Our results (see Fig. 1) showed that the supported catalysts reached their maximum activity (for the PdO phase) at very similar temperatures, suggesting PdO started to decompose at the same temperature on both alumina and zirconia carriers. The temperature for the maximum activity for the catalyst consisting of a mechanical mixture of bulk PdO and zirconia support, however, is lower. The previous TGA results [21] indicated that, in flowing air, the PdO decomposition temperatures for the catalyst supported on alumina differed significantly from those supported on zirconia or unsupported PdO. Our reactivity results are not necessarily in contradiction with those reported here because in our experiments the PdO decomposition temperatures were measured in presence of methane, which may be involved in the reduction process, while the TGA experiments were performed in presence of oxygen, without methane.
On the other hand, the onset of the activity decay on the heating ramp does not necessarily coincide with the appearance of metallic palladium on the surface. Voogt et al. [44] using an XPS technique gave evidence that the initial stage of the thermal reduction consists of the formation of a metallic core, whose size increases linearly with the time at constant temperature until the last surface oxide monolayer, so the catalyst exposes an oxide surface until the last stage of reduction. The catalytic activity of the catalyst particle at intermediary stages of reduction could be different from the one of the completely oxidized catalyst. In our work [1] on samples quenched at incipient reduction conditions, an amorphous surface layer of an unidentified phase was observed using high resolution TEM. The presence of such a surface layer is likely to influence the catalyst activity and may be responsible for the deactivation of the catalyst at an early stage of PdO reduction. In fact, amorphous PdO has been shown to have lower activity for methane oxidation at low temperatures [15]. Therefore, the TGA technique is adequate to determine the catalyst phase changes, but these do not necessarily strictly correlate with the changes in catalyst activity. Also, if performed in absence of methane, the reduction temperatures observed in TGA experiments could be higher than the actual values at reaction conditions.

Figure 1. Temperature programmed reaction profiles for catalysts supported on different carriers. Closed symbols are for heating up cycle and open symbols are for cool down cycle.

The large difference in the reduction temperatures observed between the supported and unsupported catalysts suggests an important effect of the PdO particle size on the reduction temperature. Previously reported TGA results [21] did not verify whether the PdO particle size of the catalysts supported on different carriers was constant, therefore the reported differences could also be caused, at least partially, by dispersion differences.

After the first reduction/reoxidation cycle, the methane combustion activity of the catalyst comprised of the mechanical mixture of PdO and zirconia dropped significantly compared with the supported ones. The activity of the supported catalysts dropped much less than the mechanical mixture, the extensive drop of activity correlates rather with the particle size than with the support composition. The activity drop correlates with the increase in catalyst particle sizes ranked as Mechanical Mixture > Zirconia Supported ≥ Alumina Supported.
On the cooling down cycle after thermal reduction the activity decreases and then increases at different temperatures for the supported catalysts. These differences suggest different rates of oxidation for metallic particles deposited on different carriers. This conclusion results from the significant difference observed between the supported catalysts, which have uniform palladium loadings and particle sizes. Moreover, this is the only significant difference observed between the supported catalysts in the present study. Support interactions with the metallic palladium phase were observed to be stronger than for the oxide phase. The significantly lower temperature for the onset of reoxidation of the mechanical mixture is most likely due to a particle size effect. The palladium reoxidation onset temperatures observed in our TPR experiments, however, are in disagreement with those reported by Farrauto et al. [21], despite the higher oxygen partial pressure in their experiments. Both supported catalysts started to recover their activity at higher temperatures than those reported from TGA results. These findings suggest that the catalytic activity strongly increases at the initial stage of catalyst oxidation when the weight gain is too small to be detected in TGA. This interpretation is also in agreement with our recent pulse experiments [8] that showed higher catalytic activities for partially reduced surfaces, and the results from quenched catalysts interrogated with XPS [24]. In addition, TGA experiments measure bulk changes that should not necessarily correlate with activity. Later experiments showed oxygen uptake is inhibited by the presence of methane, again suggesting that TPO experiments can not be used to directly correlate reactivity behavior.

On the other hand, the reduction – reoxidation temperatures are observed to be particle size dependent, which suggests oxygen internal diffusion limitations, mainly for the reoxidation process. However, the catalyst activity recovers before the completion of the reoxidation process, which suggest that the reoxidation proceeds from the surface toward the particles bulk, as proposed by other authors [20, 28].

Higher catalytic activity was observed for supported PdO particles on cooling down from temperatures that did not cause the thermal decomposition of the PdO phase, thus without a reduction/reoxidation cycle. The activation mechanism could consist of a slight reduction of the PdO phase by methane, which generates surface reduced sites/oxygen vacancies, as proposed by Fujimoto [45,46]. Muller and co-workers [47] showed using catalysts containing $^{18}$O isotope that methane is oxidized with PdO lattice oxygen generating oxygen vacancies that are replenished with oxygen from the gas phase. Recent results of Au – Yeung [10] also gave evidence of lattice oxygen extraction at the early stage of methane combustion reaction. This is consistent with both constant activity in time at constant temperature and the suppression of the activation effect after long term exposure to oxygen at room temperature. The long time constant for the deactivation at RT suggest that the reduced site consists rather of surface Pd$^0$ clusters than of pairs Pd$^{2+}$ – oxygen vacancy.

The constant activity with catalyst time on stream at high temperatures, is attributed to its good sintering resistance, which is also demonstrated by the catalytic activity vs. reaction temperature plot for both heating and cooling ramps between 673 and 953K. This behavior is most likely an effect of the strong interaction between the dispersed phase and the support, which impedes particles sintering, in agreement with previously reported high temperature stability of zirconia supported PdO particles [41].

It can be concluded that the support does not affect directly the catalyst activity in either the oxide phase, or metallic phase. It influences the temperature range of the PdO phase stability, and, therefore, the activity hysteresis gap and temperature range. However, the palladium oxide particle size also influences the oxide phase stability.

Oxidation of metallic Pd has been intensively studied by many groups of investigators over the last 20 years [1,20,21,27,39,41]. Several different Pd/oxygen structures have been reported for the system under different conditions. At temperatures below and up to room temperature and oxygen pressures on the order of 10^3 torr dissociative adsorption of oxygen on Pd(111) surface leads to 0.25 ML saturation coverage. The initial sticking coefficient was estimated at about 0.3 and the adsorption energy of oxygen on the surface near 55 kcal/mole [48]. The formation of bulk PdO was observed only at about 675-975K in air or 1 atm oxygen [33,49,50]. In one atmosphere air the crystalline PdO state is thermodynamically stable at temperatures below 1046K, suggesting that PdO formation over a large range of temperatures experienced in practical applications is kinetically controlled. Legare et al. [50] used XPS, UPS and AES techniques to study the interaction of oxygen with Pd (111) and polycrystalline palladium in a wide range of experimental conditions. At room temperatures and oxygen pressures about 10^4 torr, only oxygen adsorbed on the catalyst surface was observed. At about 10^4 torr and elevated temperatures (about 575K), penetration of oxygen into the "subsurface layers" of Pd crystal was observed in XPS spectra. This is consistent with STM studies discussed below where a mixed PdO surface layer was observed. The crystalline PdO phase was observed only with atmospheric pressure O_2 at 625K. Ho et al. [51] studied the interaction of oxygen with alumina-supported palladium at various metal loadings. The extent of oxidation was found to increase in three steps with increasing temperature corresponding to adsorption on the surface of Pd crystallites at ambient or lower temperatures, penetration of oxygen into the sublayer as the catalyst was heated above room temperature, and formation of palladium oxide crystallites at around 775K.

Catalyst oxidation and redispersion was investigated in this work [3] by using STM to follow the interaction of O_2 and NO_2 with a Pd (111) single crystal at 575K. Nitrogen dioxide was used because it is a more effective oxidant than O_2. Several different surface phases were observed with both LEED and STM. At a coverage of 0.25 ML (1 ML = 1 O atom/surface Pd atom), a (2x2) chemisorbed layer of oxygen atoms was observed. At oxygen coverages between 1.0-1.8 ML, complicated LEED patterns were observed that could be understood in terms of the superposition of two ordered surface structures observed in STM images. In STM movies, ad-islands were observed to form as the oxygen coverage was increased into this regime, suggesting that oxygen atoms penetrate the surface, forming a mixed Pd-O surface layer with a reduced Pd atom density; the liberated Pd atoms, along with O, form the islands. The islands display a different structure than the original terraces; neither structure, however, corresponds to any crystal plane of bulk PdO, indicating that there are states intermediate between Pd and PdO [52]. TPD results suggest a bond strength intermediate between O adsorbed on Pd and PdO. At higher oxygen coverages, the LEED pattern faded and a low temperature shoulder developed in TPD traces and rough clusters appear on the surface. XPS and TPD work on Pd (110) by Bondzie, and coworkers [53] indicates that this shoulder is associated with bulk PdO decomposition. These results are consistent with the mechanism in which dispersed Pd-O phases form over the metallic Pd surface as the transition between phases occurs.

The combined results suggest that Pd (111) oxidation proceeds through a three step mechanism: 1) rapid adsorption that stops at 0.25 ML of atomic oxygen; 2) oxygen penetration into the surface accompanied by island growth leading to the formation of two phases that are
intermediate between Pd and PdO; 3) formation of bulk PdO. The driving forces for this mechanism can be described as follows. Assuming second order desorption, the O₂ desorption peak temperature at coverages less than 0.25ML suggests a heat of adsorption of roughly -50.2 kcal/mol [1], which is significantly higher than the -25.65 kcal/mol (at 1050K) heat of formation of PdO. Thus, as expected, initial exposure of either NO₂ or O₂ to Pd(111) results in oxygen adsorption. Increasing the coverage of the adsorbed layer beyond 0.25ML requires compression of the (2x2) layer that results in repulsive adsorbate-adsorbate interactions that reduce the heat of adsorption below the heat of formation of the oxide. Therefore, at higher coverages, oxide formation is favored. The Pd-Pd nearest neighbor distance in PdO is 0.305nm versus 0.275nm in Pd, thus oxidation requires expansion of the Pd surface; the resulting compression is relieved by ejecting Pd atoms from the terraces. At this stage, a Moiré pattern seen in the STM images, and multiple scattering seen in the LEED patterns, indicate that single oxidic, or alternatively reconstructed layers form on top a unreconstructed Pd(111) surface. As a result, the oxygen atoms and the Pd atoms in these layers interact with underlying Pd atoms that are bound to no other oxygen atoms. Therefore, it is not surprising that that oxygen atoms are more strongly bound in these layers that in the bulk oxide. Further, since the oxidic layers are so thin, interactions with the substrate and surface effects determine the structure, and so the layers exhibit structures that are distinct from either Pd or PdO. As the oxygen coverage increases, bulk effects become important and the O-Pd bond strength becomes characteristic of the bulk oxide.


There is much interest in the reactivation of the catalysts as it is cooled and reoxidized from the metallic state as this process may have direct implications for the non-steady state fluctuations in activity noted in practical catalytic combustion systems. Two interesting questions relate to 1) why the reoxidation is inhibited on cool-down and how this is related to the mechanism of reoxidation and 2) how activity changes as a function of surface structure on cool down. We have shown that activity decreases until some small amount of surface oxide is formed and then increases continuously to a level higher than observed on the heat-up cycle. If reoxidation occurred by a shrinking core mechanism as has often been suggested activity should recover to the heat-up level when several mono-layers of oxide are formed. Thus the mechanism for reoxidation directly controls the reactivity behavior observed.

Recent work on this grant has addressed the self-limiting oxidation observed during cool down of Pd in air (or under lean methane oxidation conditions). For example, it is found that reoxidation of Pd is delayed, upon cool down, to temperatures below which PdO should be stable based on bulk thermodynamics. Thus, even though PdO decomposes to Pd when heated above 1068K, during cooling, re-oxidation does not commence till the catalyst is cooled below 923K. At temperatures below 923 K, oxidation begins during cool down, but if the catalyst is held at a constant temperature the oxidation to PdO is not complete, but reaches a self-limiting amount of oxide. This behavior is observed during reaction rate measurements, where the reactivity increases but reaches a stable value that is between that of the fully oxidized catalyst and the
reduced catalyst. Our work has been directed at understanding the morphology of the oxide under conditions where the rate of oxide formation has ceased even though thermodynamics favors complete oxidation to PdO. What is unusual about this oxidation process is that if the temperature is lowered, oxidation commences again and reaches another self-limiting state.

This inverse dependence on temperature, causing greater extents of oxidation at lower temperatures, has been observed during reaction studies as well as by oxygen uptake measurements. We have confirmed this phenomenon by measurements within a thermo gravimetric analyzer (TGA). To study the morphology of these samples, separate experiments were performed in a tube furnace where the samples were quenched after cooling in air to temperatures in the range of 873 K – 923K. We find, by TEM, the coexistence of Pd and PdO domains in some of the particles quenched from the fixed temperature region where oxygen uptake is slow. This indicates that the self-limiting oxidation is not caused by the growth of a surface oxide that limits oxidation by slowing down diffusion, but rather suggests that the Pd metal surfaces are passivated possibly by a larger or stronger bound oxygen as suggested by McCarty [26,27]. As temperature is lowered, the thermal stresses in the passivation layer may cause a break down of the passivation layer, lead to nucleation of additional oxide domains, and an increase in oxide content.

We have contrasted the behavior of Pd during oxidation with that of Ni, which shows a conformal growth of NiO on Ni. The oxidation of Ni follows a shrinking core of metal with a growing surface oxide, a behavior that is very different from that of Pd.

We propose that formation of the PdO phase occurs through the interaction between the Pd atoms, migrating over the surface and the adsorbed oxygen: \( \text{Pd}^{+} + \text{O}_{\text{ad}} \rightleftharpoons \text{PdO}^{+} \), rather than by a direct incorporation of surface oxygen into the Pd layer. This is consistent with the work of Altman et al. [52] described above using LEED and STM where small islands of intermediate Pd-O phases were observed on the surface of metallic Pd(111) surface under the NO equivalent pressure of 760 torr oxygen at 500K. Thus reoxidation occurs through a nucleation mechanism.

Further evidence for the “patchy” oxidation comes from our recent studies [1,39]. Oxidation of Pd at low temperatures resulted in discrete patches of PdO detected by TEM. XPS showed the presence of both Pd and PdO on the surface for selected oxidation conditions. Figure 2 shows an example of such a particle. Since quenching would create more, not less oxide, the existence of two phases is confirmed. The redox reaction between methane and oxygen over the surface creates the conditions for the dynamic equilibrium between the Pd and the PdO phases. Adatoms of Pd\(^{0}\) are continuously oxidized by the oxygen adsorbed on the metallic surface, while the PdO clusters are reduced by the reaction. In support of this idea, the reoxidation temperature on the cool down cycle is somewhat higher in the presence of the methane/air reaction mixture than in air despite the observation in this work and others that at low temperatures methane impedes gas phase oxygen exchange with the surface. Oxidation of the palladium surface can, therefore, be considered as a nucleation phenomenon. Dimers and small PdO\(_{\text{cr}}\) clusters continuously appear on the surface, though the growth of the PdO phase can start only when the lifetime of such cluster is long enough for other Pd adatoms to be captured and oxidized on its surface. The lifetime increases as temperature decreases. This mechanism of a dynamic equilibrium suggests that both the metallic and the oxidized phases of palladium exist for long times at the surface of the catalyst particle over some range of temperatures. Furthermore, it is likely that the newly formed patches of the PdO phase initially do not have the crystalline structure. Because, under reaction conditions, PdO is continuously reduced to metallic Pd, no extended layer of crystalline PdO can form over the surface of the metallic particles when
reoxidation starts. PdO would preferentially appear as patches over the surface of the metallic particle. Fully oxidized particles show many surface pitches with crystalline domains of about 5 nm, creating an apparent redispersion and consistent with a nucleation mechanism. This phenomenon may be responsible for an increase in the apparent catalyst activity after the in situ hydrogen reduction or on the cooling cycle after previous reduction at temperatures above 1175K. Under these conditions, the activity decreases as the PdO phase is reformed. Reoxidation is slow and oxide growth is patchy as described above.

![Figure 2. TEM image of a catalyst sample quenched at 933K.](image)

Our new data also shows evidence that the increase in activity seen on reoxidation either when cooling or after H₂ treatment is due to the coexistence of phases and not just a redispersion of PdO. TEM analysis of Pd catalysts just a few minutes after negative activation show mainly Pd particles with little surface roughening. No PdO is observed by TEM but both Pd and PdO are shown to be in the surface region by XPS, a surface sensitive technique. Since the quenching process could only result in more not less oxide this illustrates that negative activation is seen before significant bulk oxide is formed. Recent work by Altman for CO oxidation viewed by STM also shows an intermediate state of the catalyst to be most active.

**Contribution of lattice oxygen from the PdO phase and from the support in the methane combustion** (paper “Contributions of lattice oxygen in methane combustion over PdO-based catalysts” submitted to J. Catal., 2000 – Appendix I)

Early pulsed reaction studies of Müller et al. [47] employed zirconia supported PdO catalysts labeled with Pd¹⁸O, prepared from amorphous Pd – Zr alloys. These authors proposed that, both at 573K and 773K, the combustion reaction proceeds partly via a redox – Mars and van Krevelen – mechanism, but that the overall conversion is determined by the interplay between the surface reaction of “adsorbed” reactants and the redox mechanism. This study also reported an important influence of the oxygen isotopic exchange of carbon dioxide between the gas phase and the Pd¹⁸O surface on the distribution of the carbon dioxide isotopomers, while the
isotopic exchange of gas phase oxygen was negligible. In a more recent paper [54] these authors concluded that the abstraction of hydrogen atoms from the adsorbed methane species is a "normal surface reaction", whereas the formation of oxygen – carbon bonds is more controlled by a redox mechanism involving lattice oxygen.

Based on turnover rate measurements of the methane combustion reaction performed over zirconia-supported catalysts, Fujimoto [45] proposed a set of elementary steps describing the reaction mechanism. In the proposed mechanism, the catalytic site is considered as a surface oxygen vacancy or coordinatively unsaturated Pd site on the surface of PdO crystallites, depicted generally by "Pd-PdO site pair". In a later work [46] these authors concluded that the overall mechanism resembles Mars – van Krevelen reduction–oxidation pathways in which "carbon atoms in the gas phase or physisorbed CH$_4$ interacts with coordinatively unsaturated Pd sites on the surface of PdO crystallites and H atoms are abstracted sequentially from adsorbed CH$_4$ by neighboring Pd – O surface species to form surface hydroxyl groups (Pd – OH)" [46]. The authors assert the proposed mechanism avoids the need for the coexistence of a separate Pd metal phase in atomic contact with PdO$_x$ during methane oxidation.

The mechanism proposed by Fujimoto [45,46] was further studied in the more recent work of Au-Yeung et al.[10]. They performed the methane combustion reaction over zirconia-supported Pd$^{16}$O particles using continuous flow of a reaction mixture containing $^{16}$O$_2$ and $^{18}$O$_2$ in equal amounts, in the 500–600 K temperature range. These authors observed negligible oxygen scrambling but important CO$_2$ scrambling during methane combustion. They also suggested that "lattice" oxygen is used more efficiently than oxygen from the gas phase in methane combustion.

None of the above mentioned studies [10,45-47,54] measured the distribution of oxygen isotopes in the water molecules produced in the methane combustion reaction in a systematic manner. In addition, the catalysts used in the previous studies were all supported on zirconia carriers, a support with relatively high oxygen mobility at moderate and high temperatures [55]. Therefore oxygen can be exchanged between the PdO and the support and influences the distribution of oxygen atoms in the reaction products.

The catalysts employed in our study were pure PdO (99.999% of purity) and zirconia supported PdO (3% wt. as Pd). The average PdO particle size of the fresh supported catalyst determined from XRD was 10 nm. The reaction mixtures used consisted of 1% methane, 4% oxygen either as $^{16}$O$_2$ or $^{18}$O$_2$, and helium balance feed in pulses at 80 seconds time interval.

The only reaction products detected following reaction mixture pulses over the catalyst were carbon dioxide and water. Oxygen, carbon dioxide and water isotopomers were monitored using the mass selective detector. The relative distribution of $^{18}$O atoms in the same product was determined using the mass spectrometry analysis, the carbon material balance and conversion being determined from gas chromatographic analysis. Therefore, in the mass selective detector samples were analyzed for ions with masses 18 and 20 for water, masses 32, 34 and 36 for oxygen, and masses 44, 46 and 48 for carbon dioxide isotopomers. The distribution of $^{18}$O among reaction products at different experimental stages is given in the figures in Appendix I.

The first labeled reaction mixture pulse over a Pd$^{16}$O catalyst at all temperatures studied produced predominantly C$^{16}$O$_2$, suggesting lattice oxygen is predominantly used for methane combustion. For the unsupported PdO catalyst at all temperatures excluding the lowest (600K), the relative fraction of C$^{16}$O$_2$ decreased rapidly with the number of pulses and then changed to a lower, constant slope, maintained up to the end of the labeled reaction mixture pulse series. It was also noted that a longer (3 minutes) time interval between pulses number 17 and 18.
produced a slight increase in the C\textsubscript{15}O\textsubscript{2} relative fraction. This increase is rapidly lost and is due to an increase of surface \textsuperscript{16}O concentration caused by bulk oxygen migration towards the surface. For all conditions of this study the methane conversion was constant for all pulses at a fixed temperature even though the isotopic distribution changed markedly indicating a single mechanism and a single type of oxygen used. As temperature increases, the amount of \textsuperscript{18}O in the carbon dioxide increases steeply followed by a much slower increase at higher temperatures, typical of a transport limited process. This suggests that labeled oxygen uptake is limited by exchange with the bulk at higher temperatures. The concentration of H\textsubscript{2}\textsuperscript{18}O increased slowly as the pulse number increased and as temperature increased. The isotopic composition of water resulting from methane combustion over Pd\textsuperscript{16}O catalyst remained predominantly H\textsubscript{2}\textsuperscript{16}O at a large number of pulses in contrast to the quickly increasing \textsuperscript{18}O content in the CO\textsubscript{2} even at the higher temperature of this study.

In order to determine both the overall oxygen exchange and to qualitatively assess the distribution of oxygen isotopes with the depth from the particle surface toward the bulk, the catalyst was reduced after reaction at the reaction temperature using either diluted methane or diluted hydrogen.

For the unsupported catalyst, as the temperature increases the uptake of gas phase oxygen onto the catalyst increases. This is consistent with the increase in \textsuperscript{18}O-containing isotopomers in CO\textsubscript{2} and the increase of the H\textsubscript{2}\textsuperscript{18}O concentration in reaction products with the reaction temperature. Another interesting observation is that, assuming a “layer by layer” reduction mechanism both for reduction with methane and hydrogen pulses, the \textsuperscript{18}O concentration gradient between bulk and surface is initially small, but then increases with the temperature, suggesting that \textsuperscript{18}O exchanged becomes limited by penetration of \textsuperscript{18}O into the bulk. A final interesting observation is that the distribution of water isotopomers produced during the reaction is similar to the one observed in reduction experiments, suggesting the composition of water resulting from the reaction reflects the bulk composition of the catalyst particle. For reduction with diluted methane (665K and 745K), the conversion resulting for the first reducing pulse equaled the one observed with the last reaction mixture pulse. When hydrogen was used as reductant, because of its high reactivity for PdO reduction the total pulse is consumed, consistent with the equal number of hydrogen pulses consumed to reduce the catalyst after reaction at different temperatures (600K, 625K, 670K and 700K).

The zirconia-supported catalyst behaved similarly to the unsupported one at the lowest temperature of these experiments. However, as temperature is increased, the distribution of carbon dioxide isotopomers shows significant differences. The most important difference between the supported and unsupported catalysts is that at higher temperatures the amount of \textsuperscript{16}O in the reaction products is considerably higher for similar amounts of methane converted. This suggests an important contribution of the support to the \textsuperscript{16}O pool of the PdO phase. The increase of the \textsuperscript{16}O content in the reaction products as the reaction temperature increases is most likely due to an increase in the oxygen exchange rate between the PdO particles and the zirconia support and follows the temperature dependence observed by Duprez et al. [55] for oxygen mobility on zirconia. The important contribution of the support to the oxygen pool of the catalyst is also suggested by the distribution of water isotopomers. Similar to the CO\textsubscript{2} result, the \textsuperscript{18}O-containing isotopomer is more abundant at lower temperature. The oxygen exchange with the support impedes \textsuperscript{18}O exchange to the bulk. This is confirmed by the pulsed reduction experiments performed after the reaction studies, as discussed below.
The isotopic distribution for carbon dioxide and water resulting from reduction experiments for the catalyst where the reaction is carried out at 600K showed $^{18}$O-rich reaction products suggesting the PdO surface is rich in $^{18}$O. Further pulses reduced the bulk and showed much higher $^{16}$O content. By contrast, for the catalyst where the reaction was carried out at 700K the oxygen exchange rate between the support and PdO particles is fast so that the oxygen isotopes at the surface are equilibrated with the support (having a large reservoir of $^{16}$O). The $^{18}$O exchange from the gas is much slower than the exchange from the support, so that the bulk and surface are also equilibrated. Note that the PdO particle size is much smaller than the grain size in the pure PdO catalysts, which affects the equilibration time. Therefore, for all the reduction pulses at the higher temperature of 700K the isotopic composition of the reaction products changes insignificantly with pulse number suggesting a uniform distribution through the catalyst. In contrast with the unsupported catalyst, $^{18}$O at the surface was lower at higher temperatures.

Several conclusions derived from these results:

- The differences in the labeled oxygen atoms distribution between water and carbon dioxide are not due to different oxidation mechanisms for hydrogen and carbon, respectively, as was previously suggested in other studies [47]. Our results clearly indicate that, because of a lower rate of water desorption relative to the rate of isotopic equilibration of surface and bulk oxygen, and because hydrogen samples the bulk, the water molecules produced in the combustion reaction reflect the composition of the bulk catalyst. Carbon dioxide is desorbed more rapidly and it is reflective of the isotopic composition of the surface.

- Surface hydroxyls resulting from methane dissociation at the PdO surface impede the oxygen uptake by the catalyst. In pulsed experiments performed at temperatures below 745K, because of the longer residence time of hydroxyl groups at the surface, following water desorption the oxygen partial pressure in the gas phase is too low to allow a significant oxygen uptake onto the reduced surface. As temperature increases, the rate of water desorption increases significantly, as well as the oxygen uptake. Therefore, the inhibitory effect of water molecules on the activity of the PdO catalyst for methane combustion can be explained, at least partially, by the mechanism discussed above.

- The zirconia support contributes significantly to the oxygen pool of the PdO phase available for the methane combustion. Experiments performed with isotopically labeled reaction mixture at two temperatures showed that at 700K the exchange of oxygen between support and PdO is very rapid.


From the point of view of the reaction mechanism, Fujimoto et al. [45,46] proposed a set of elementary steps in which the catalytic site is an oxygen vacancy or coordinatively unsaturated Pd site on the surface of PdO crystallites. They concluded that the mechanism resembles the Mars and van Krevelen mechanism and avoids the need for the coexistence of a separate Pd metal phase in atomic contact with PdOx during methane oxidation [4]. A possible methane activation step is the dissociative adsorption of methane on a surface Pd – O pair as proposed by Broclawik et al. [56]. It should be noted that the reaction order with respect to oxygen reported by many investigators is positive and near zero. Vacancy development,
especially under conditions where water is desorbed between pulses (pulsed experiments above 725K), would be expected to be negative order with respect to oxygen. Au-Yeung et al. [10] used an isotopically labeled technique to investigate the methane oxidation pathways on PdO catalysts. They concluded the lattice $^{16}$O in PdO is more efficiently used in methane combustion than labeled $^{18}$O atoms from the gas phase. Their results suggested reoxidation is slow and from an estimated $^{16}$O balance, either the bulk and surface are partially reduced, or oxygen exchange with the zirconia is fast. Based on results obtained with pulsed studies over zirconia-supported Pd$^{18}$O catalysts prepared by oxidation of palladium-zirconia alloys, Muller and co-workers [57] concluded that the combustion reaction proceeds partly via a redox mechanism in which the abstraction of hydrogen atoms from the adsorbed methane species is a “normal surface reaction”, whereas the formation of oxygen–carbon bonds is controlled by a redox mechanism. Their assumption was based on the differences observed between the distribution of labeled oxygen atoms in water and carbon dioxide products.

The existence of different reaction mechanisms for the oxidation of carbon and hydrogen, respectively, would require the existence of two different types of oxygen at the catalyst surface. The crystal structure of PdO is a useful starting point in considering the types of sites that could be available for reaction on a PdO catalyst surface. Palladium oxide crystallizes in a tetragonal structure with lattice constants a = b = 0.305 nm and c = 0.534 nm at room temperature; Pd atoms are located at (0, 0, 0) and (0.5, 0.5, 0.5), and oxygen atoms at (0.5, 0, 0.25) and (0.5, 0, 0.75). Each Pd atom is coordinated to four O atoms in a square planar configuration while each O atom is surrounded by four Pd atoms in a tetrahedral pattern. Cleaving the structure perpendicular to [001] and [110] results in the least corrugated surfaces, and thus (001) and (110) surfaces are expected to be favored. In considering the surface models, a couple of points become immediately obvious. First, both surfaces expose only a single type of oxygen species: an oxygen atom bridge bound to two Pd atoms. Although much has been made in the literature about potential differences between "lattice" and "adsorbed" oxygen species, considering these models, it is difficult to envision an oxygen species in a site other than the bridge site. It should also be noted that the (100) and (010) surfaces also expose only a single type of oxygen species. The second point is that both surfaces are polar and thus must reconstruct to maintain charge neutrality. There has been no work reported on the surface structure of PdO, however, other oxides and binary compounds (such as halides [58] and III-V semiconductors [59]) maintain charge neutrality through ordered vacancy structures. Along these lines, removing half the surface oxygens from the bulk terminated PdO (001) and (110) surfaces would create charge compensated surfaces. Although this creates arrays of oxygen vacancies, the surfaces are fully oxidized in that all the surface Pd atoms are formally in a 2+ oxidation state. As a result, oxygen cannot adsorb at the vacancies without oxidizing the surface Pd atoms beyond the 2+ oxidation state. Considering that CH$_4$ combustion is often carried out under conditions that are near the thermodynamic border between Pd and PdO, adsorption on these vacancy sites under reaction conditions seems unlikely. Along the same lines, oxygen desorption from the charge compensated surface would require reduction of surface Pd atoms; oxygen readsorption would then reoxidize the Pd atoms to Pd$^{2+}$. While more massive reconstruction cannot be ruled out and defects such as steps and crystallite edges can create additional types of sites, the bulk crystal structure suggests only a single potential site for surface oxygen. If the edges and defects controlled reactivity, the reaction would be structure sensitive with small particles showing higher reactivity. This is not the case experimentally as particles less than 10 nm have been observed to show lower reactivity.
Although a single form of oxygen is likely responsible for reactivity at the conditions of our experiments, these results do not rule out the possible role of mixed phases under some (especially transient) reaction conditions. The experimental results presented here, however, indicate that oxygen migration in bulk PdO can be fast compared to reoxidation from the gas at low temperatures. Studies of the oxidation of metallic Pd indicate that the reaction can be slow [10,57]. The above arguments suggest that Pd and PdO can coexist for extended periods at certain temperatures and oxygen pressures, which is not thermodynamically possible if equilibration with the gas phase is rapid. We also have shown that during methane oxidation reaction, surface reoxidation/oxygen exchange with the gas phase is slow. At low temperatures the rate of $^{18}\text{O}_2$ uptake is slow and the exchange is limited by the surface reaction. In earlier work using high resolution transmission electron microscopy (HRTEM) we observed that in transient conditions the surface can likely consist of a patchy array of phases; it is also consistent with previous TPD and STM results of Zheng and Altman [3] that indicate a sequence of four phases during Pd oxidation, confirming at least one stable intermediate state. Along these lines, at any point in time the condensed phases can be described by oxygen – palladium mole fractions. Since both the miscibility of oxygen in Pd and the oxygen deficiency of PdO are limited, separation of the Pd and PdO phases will occur. The mixed Pd-O surface would exist at the interface between the two bulk phases. The phase with the lowest surface tension would tend to completely encapsulate the higher surface tension phase. Since oxides typically have lower surface tension than metals, reduced Pd clusters formed during the reaction of methane with lattice oxygen at the PdO surface are likely to be encapsulated by the bulk oxide phase. The encapsulation mechanism likely consists of bulk oxygen diffusion towards the surface, thus in equilibration of the concentration of the vacancies between surface and bulk. This is consistent with our experimental observation that, at certain operating conditions, oxygen equilibration between the condensed phases can be fast compared to equilibration with the gas phase. Hence, Pd and PdO may coexist for an extended duration, even at high temperatures. These factors may affect reactivity when the catalyst is reduced and then exposed to reaction mixture.

The most important conclusion is that, although much has been made in the literature about potential differences between lattice and adsorbed oxygen species at the PdO surface, based on thermodynamic considerations we showed that the most favorable surfaces (001) and (110) expose a single type of oxygen species: an oxygen atom bridge bound to two Pd atoms. At our experimental conditions the reactivity data with labeled oxygen shows that this one form of oxygen is responsible for the oxidation of the carbon and hydrogen in the methane.


Water, CO and CO$_2$ which are produced in the reaction of methane oxidation can also affect the activity of the catalyst. Ribeiro *et al.* [29] concluded that the dependence of the activity for methane oxidation over Pd/zirconia on water was negative first order over the entire range of conditions expected under actual operation. Earlier work by Cullis *et al.* [35] showed that water inhibits methane oxidation on palladium-based catalysts and that this deactivation is only partially reversible. The poisoning effect of water was proposed to be due to the formation of
palladium (II) hydroxide, which is not dehydrated without the loss of oxygen. This was also suggested by Burch et al. [60] in a recent study of C-H bond activation. They suggested that at moderate temperatures (below 725K) the breaking of the OH bond in the hydroxide is the rate-limiting step for methane oxidation on PdO consistent with our recent pulsed reaction studies with water [61]. Many of the apparent activation energy values reported in the literature, however, did not account for this inhibition effect and experiments were not carried out under differential reactor conditions with respect to water.

The influence of water on the catalyst activity is also affected by the type of support. For HSA γ-alumina supports, unrecoverable water poisoning was observed by many investigators [1,29,62,63]. In our experiments with Pd supported on LSA α-alumina, the water poisoning was found to be fully recoverable albeit over an hour time scale. Rare earth additives have been shown to improve the catalyst performance in the presence of water [63].

Another important point is that water poisoning is not fully understood especially with respect to support additives and the kinetics of poisoning. A recent paper by van Giezen et al. [36] points out that water poisoning can bias the apparent activation energy measured when starting with a dry reaction mixture since the reaction is not carried out differentially with respect to water. This is a very important point as a “wet” activation energy has been measured to be as much as twice as much as that of the normally reported “dry” value. The authors derive a relationship for the apparent activation energy for the dry feed $E_{\text{dry}} = 1/(1-n) E_{\text{app}}$ where n is the reaction order, with respect to water, and $E_{\text{app}}$ is the activation energy under true differential reactor conditions, (i.e. wet). This relationship, however, is only valid if the reaction responds immediately to changes in water concentration and if the order with respect to water is independent of both temperature and water content. We [5], Cullis et al. [35] and Burch [61] have found that the catalyst does not respond instantaneously to changes in water concentration. Pulsed experiments show no water poisoning effect above 700-725K whereas continuous TPR experiments show strong water poisoning up to 925K and higher. When water in the reactant mixture over the catalyst is significantly reduced, say, for example, by a decrease in temperature yielding a decreased conversion (or by shutting off an external water supply), recovery to the unpoisoned conversion level can be very slow (on the order of hours) and is sensitive to the identity of the support [5]. In addition at low temperatures in the presence of water activity is strongly influenced by heating rate. In pulsed experiments [7], water poisoning was found to become negligible at temperatures above 725K (see Figure 3), while in continuous (TPR) experiments at 5K/min water poisoning was observed at temperatures as high as 925K. Using the equilibrium assumption and the equation for dry versus wet apparent activation energy presented by Van Giezen et al. [36], changes in apparent activation energy predicted stronger water poisoning as temperature is increased, a conclusion that is contrary to observations from pulsed reaction experiments [7,61]. For example, Burch et al. [61] reported no water poisoning at temperatures above 725K. There may also be a particle size component on the degree of water poisoning.

It should be noted that when the formula is used to try to correct the activation energies reported in the literature the spread in activation energy is retained. In addition, correcting some of the data results in unrealistically high activation energies (>80 kcal/mol) suggesting that the assumption used to develop the equation do not hold for all of the experimental conditions covered. As noted above, two assumptions have been shown to breakdown experimentally. First, water absorption/desorption is not equilibrated and the water poisoning affect in pulsed experiments is not observed above 725 K [7].
Our pulsed experiments show evidence that at low temperature, the water resulting from reaction remained adsorbed at the catalyst surface for as long as 30 minutes in a dry carrier gas environment. Therefore, pulses injected at short time intervals showed a lower conversion than those injected at time intervals longer than 30 minutes. The effect of water on the activity of the catalyst also might suggest that experiments to measure catalyst activity should be run with enough water such that the total water concentration would not change by more than 10% at different levels of methane conversion. It is not necessarily simple, however, to correct for water poisoning as the reaction order with respect to water has been shown to vary with temperature, amount of poison and type of support [5,7,61].

Modeling of transient activity, therefore, will require knowledge of the kinetics of poisoning. In addition, a survey of literature data for the apparent activation energy at low conversions and temperatures yields a “dry” apparent activation energy of approximately 40K cal/mol. Assuming that the reaction order with respect to water is -1, the above equation would predict a “true” activation energy of 80K cal/mol which yields an unrealistically high pre exponential factor and is inconsistent with physical parameter estimation. This means that “wet” reaction data may not be useful in predicting reactor performance and will not reflect transient performance and may even be flawed for some steady state regimes. Our recent work suggests that when reactions are carried out in pulsed mode, the reaction order with respect to water varies with both temperature and water concentration.


Among other issues, activity as a function of oxidation state for Pd-based catalysts is not well understood, especially with respect to mixed states and transient operation. Oh et al. [22,23] argue that the reduced Pd form is more active. Hicks et al. [28] observed that the activity of
dispersed PdO is 10 to 100 times less than that of small palladium crystallites, and these authors also observed that the oxide layer dispersed over the palladium crystallites is much more active than the palladium oxide dispersed over the alumina. Burch et al. [17,61], Farrauto et al. [20,21], Primet et al. [18,24,25] and McCarty [27] consider the metal phase to be less active or completely inactive. A recent study of our group [9] shows that metallic palladium can be more active than PdO in the methane combustion reaction at higher temperatures and at stoichiometries near one and for fuel rich conditions. For a wide range of conditions, the catalyst activity has been observed to increase as the PdO is reduced or partially reduced. Positive activity excursions have been noted by many investigators in pulsed reduction by hydrogen or methane [9,33], and the activity hysteresis and transient excursions noted in laboratory and large scale experiments cannot be predicted a priori from any published micro kinetic mechanism.

In our earlier work [5] we observed that there is lack of agreement between the palladium reoxidation temperatures observed in TGA and temperature programmed reaction (TPR) experiments and suggested that this difference may be due to the higher activity of the partially reduced / oxidized state of the catalyst. Methane combustion activity excursions were previously reported following catalyst reduction with hydrogen or methane [9,33]. Bell and co-workers [33] observed that hydrogen pulses injected in the reaction mixture stream flowing continuously over the zirconia supported PdO catalyst at temperatures in the 400 – 450K range produced a noticeable increase of the CO₂ production rate. However, after a certain number of hydrogen pulses, the catalyst activity dropped to zero, even at 450K where the activity of the catalyst before hydrogen pulses was higher than zero, suggesting that a large degree of reduction eventually produces catalyst deactivation. The authors claimed that CH₄ is not activated on PdO at low temperatures and ascribed the activity excursions to the formation of small amounts of Pd on the surface of PdO. They also claimed that the presence of metallic palladium in close contact with PdO greatly enhanced the rate of reduction of PdO by methane and argued that it occurs via a nucleation mechanism that requires the presence of metallic palladium [49]. In this research we have shown that a nucleation mechanism is likely. A nucleation mechanism followed by oxygen transport limitations form the bulk would explain the increase followed by decrease in reactivity during reduction with diluted methane. First the surface layers are completely reduced then the rate of reduction is limited by transport of oxygen from bulk to the surface. Reduction with hydrogen results in constant conversion per pulse [4]. With diluted methane pulses, however, conversion during reduction of PdO varies dramatically pulse to pulse. At low temperatures and mild reduction conditions the surface is reduced gradually. At these conditions methane conversion can increase on subsequent pulses before decreasing when the reduction process becomes limited by transport of oxygen to the surface. At high temperatures where the surface layers are completely reduced on the first pulse, conversion continually decreases because reaction is limited by transport of oxygen to the surface or by reoxidation from the gas phase.

In related work (described above) we showed that a single form of oxygen is likely responsible for reactivity at the conditions where the PdO phase is stable [4]. These results do not, however, rule out the possible role of mixed phases under some reaction conditions. Studies of the oxidation of metallic Pd indicate that the oxidation reaction can be slow [23,61]. In addition, at low temperature reaction conditions reoxidation from the bulk can be faster than from the gas phase. This creates a steady state of vacancy states. The above arguments suggest that Pd and PdO can coexist for extended periods at certain temperatures and oxygen pressures, which is not thermodynamically possible if equilibration with the gas phase is rapid. We and
other researchers have shown that during methane oxidation reaction, surface reoxidation/oxygen exchange with the gas phase is slow. Using high resolution transmission electron microscopy (HRTEM) we observed that in transient conditions the surface can likely consist of a patchy array of phases [39]. The TPD and STM results of Zheng and Altman [3] show a sequence of four phases during Pd oxidation, confirming at least one stable intermediate state. Along these lines, at any point in time the condensed phases can be described by oxygen- palladium mole fractions. Since both the miscibility of oxygen in Pd and the oxygen deficiency of PdO are limited, separation of the Pd and PdO phases will occur. The mixed Pd-O surface would exist at the interface between the two bulk phases. The phase with the lowest surface tension would tend to completely encapsulate the higher surface tension phase. Since oxides typically have lower surface tensions than metals, reduced Pd clusters formed during the reaction of methane with lattice oxygen at the PdO surface are likely to be encapsulated by the bulk oxide phase. The encapsulation mechanism likely consists of bulk oxygen diffusion towards the surface, thus in equilibration of the concentration of the vacancies between surface and bulk. This is consistent with our experimental observation that, at certain operating conditions, oxygen equilibration between the condensed phases can be fast compared to equilibration with the gas phase. Hence, Pd and PdO may coexist for an extended duration, even at high temperatures. These factors may affect reactivity when the catalyst is reduced and then exposed to reaction mixture as in the experiments described here.

An important question that needs to be addressed is whether the chemical reduction with methane generates the same state of the catalyst as the thermal decomposition of PdO. It should be mentioned that the amount of methane consumed in the experiments where pure methane was used to reduce the catalysts is below the stoichiometric amount necessary for the complete reduction of the PdO catalyst, assuming the whole amount was consumed by the palladium oxide. Moreover, the amounts of methane consumed at different temperatures were different for the same amount of catalyst: at 633K only traces of CO2 were detected, while at 663K the CO2 concentration in the reactor effluent after the first methane pulse was considerably higher, and at 763K the oxygen balance suggests the bulk catalyst is highly reduced. At 763K, although the catalyst may be fully reduced, oxygen from the support could also be removed in the presence of Pd (pure zirconia does not reduce); however, we have shown in related research [4] that exchange of oxygen between zirconia and Pd under these pulsed reaction conditions becomes fast at 700K. Consequently, the degree of the catalyst reduction with methane increases with the temperature. We proposed that, in contrast with the thermal reduction, the chemical reduction proceeds from the surface towards the particle bulk, thus forming a reduced layer on top of an oxide core.

In a separate experiment, continuous flow of 1% of methane in helium for three hours at 633K did not completely reduce the palladium oxide phase, but produced partially reduced PdO particles as observed by UV-vis spectroscopy. After this treatment the catalyst showed the same activity excursion. This suggests the energetic barrier for reduction increases with the degree of reduction, most likely because of the low diffusion rate of the bulk oxygen at low temperatures. Meanwhile, the reduced surface layer could also be less permeable for oxygen than palladium oxide, thus acting as a diffusional barrier.

Formation of CO during reduction at high temperature suggests that the oxygen species extracted by the methane molecules are available at a lower rate, likely due to diffusion limitations from the bulk. Comparing the temperature reduction profiles obtained using methane as reducing agent for catalysts pretreated at different conditions, Muller [57] proposed the
existence of several kinds of PdO having different reactivities for the reduction with methane. In agreement with the "reduced layer on top of an oxide core" proposed model, extraction of the oxygen from the subsurface layers has a higher energy barrier than that for the surface oxygen, and has a lower rate than surface oxygen depletion. Under these circumstances, the CO formed as intermediary oxidation product is desorbed from the surface before being completely oxidized. However, since at the higher temperatures required for the subsurface oxygen extraction the oxygen mobility is higher, a contribution of the oxygen from the support cannot be completely ruled out.

The catalysts that were partially reduced using methane pulses behaved completely differently in the combustion reaction when compared with the catalysts that were fully reduced by thermal decomposition of the PdO phase. The initial combustion activity of the chemically reduced catalyst was much higher than that of the thermally reduced one, but this high activity rapidly decreased to a minimum and then increased again. In contrast, the thermally reduced catalyst had a low initial combustion activity, which gradually increased to reach a plateau value higher than that observed at the same reaction conditions before reduction, consistent with the activation noted in cycled TPR experiments. The catalyst reduced with methane at 763K showed formation of carbon monoxide when exposed to reaction mixture pulses after the reduction step, despite the presence of excess oxygen in the pulses. This behavior suggests that only lattice oxygen is used for methane oxidation, and the uptake of gas phase oxygen is slow. Therefore, the amount of oxygen in the PdO layers near the surface accessible for the methane molecules at this temperature is not enough to completely oxidize the methane fragments resulted from dissociation of the methane molecules. This explanation is consistent with previous results [4] showing diffusion of oxygen from the bulk can be the rate limiting step for methane combustion.

The chemical reduction process generates a different catalytic surface that is more reactive for methane combustion, but which deactivates with the number of reaction mixture pulses injected. The chemically reduced catalyst also reoxidizes more rapidly than the thermally reduced one. This is consistent with observations that catalysts that are only partially reduced reoxidize quickly while those fully reduced show an inhibition to reoxidation when cooled. It is unclear yet whether the surface reduced layer produced by chemical reduction consists of metallic palladium or an intermediate PdO\(_x\) phase with x<1. However, the initial activity of the chemically reduced catalyst increases with the degree of reduction until reaches a maximum, after which decreases as the oxygen content of the catalyst decreases. In recent work Altman observed important changes in the CO oxidation rate with the change in the oxygen coverage of a Pd (111) surface. They reported formation of a (2x2) adsorbed structure at low temperatures and low oxygen exposures, and the coexistence of the above mentioned structure with a (\(\sqrt{5}\times\sqrt{5}\))R27° structure that forms only following long exposures at high temperatures (500K). The rate of CO oxidation increased as the (\(\sqrt{5}\times\sqrt{5}\))R27° structure disappeared, reaching a maximum at the oxygen coverage corresponding to the maximum concentration of the (2x2) adsorbed oxygen at the surface. These results are in agreement with the higher activity of the partially reduced polycrystalline catalyst discussed above.

The activity of the chemically reduced supported palladium catalyst for methane combustion has been found to experience important changes with the modification of the oxygen content of the catalyst. Slightly reduced samples were observed to be more active for methane combustion than either completely oxidized or metallic particles. This is consistent with studies showing fuel rich oxidation over PdO (under conditions where PdO is the stable phase) to have a much higher specific activity than under excess oxygen conditions. Isotopic labeling experiment
showed uptake from gas phase is slow in the presence of methane oxidation and also confirms single type lattice oxygen is used to oxidize methane.

**Synergetic effects between ceria and palladium particles** (paper “Pd–Ce interactions and adsorption properties of palladium: CO and NO TPD studies over Pd–Ce/Al₂O₃ catalysts” Appl. Catal. B, 26(2000), 241–255)

In the last few years, the use of Pd-based catalysts for three-way catalysis has increased considerably [64]. To achieve faster light-off performance, particularly for HC conversion, Pd-based catalysts offer significant advantages over the traditional three-way catalysts [65-68]. The use of Pd is considered attractive because of its ability to catalyze the oxidation of HC at temperatures significantly below that of comparable Pt-Rh catalysts, and because of its high temperature durability [69]. However, it is well known that Pd-only catalysts show insufficient NO, conversion at stoichiometric conditions [66,70]. Studies have shown that with net oxidizing conditions, Pd favors the CO₂ reaction over the CO-NO reaction - as opposed to Rh. As a consequence when using Pd the Air/Fuel window is narrowed due to the poor NO, conversion on the lean side [71]. Efforts have been focused on improving the catalytic performance of Pd.

Changes in the washcoat crystallite structure by use of perovskites were found to improve the activity of Pd [72]. The classical promotion by ceria has been extended to lanthanum oxide and other rare earth and alkaline metal oxides [70,73-75]. Supports other than Al₂O₃ such as yttria-stabilized zirconia [76] and ceria-zirconia [77] have also been used. Finally, a structure of double layered Pd catalysts was also developed and was found to improve Pd activity [67]. However, only few efforts have been devoted to understand the effect of the interactions between Pd and ceria in Pd-Ce/Al₂O₃ [78] and in Pd/CeO₂ system [79-81]. Palladium catalysts supported on alumina and ceria/alumina supports prepared by different methods were investigated by means of CO and NO temperature programmed desorption (TPD), and by pulsed CO experiments.

Although the catalysts underwent different treatments (i.e. pre-reduction, pre-oxidation or pre-aging) all the samples exposed a metallic surface after 30 minutes of flowing CO at room temperature. Therefore, the differences that appeared among the CO – TPD profiles as a function of pretreatment history are likely related to differences in the bulk composition of catalyst particles supported on different supports.

For all of the catalysts a significant fraction of the adsorbed CO desorbs as CO₂ and following NO adsorption, for all the investigated systems NO, N₂, N₂O and NO₂ were the four species detected desorbing from the surface as the temperature of the catalyst was increased, independent on the sample pretreatment history.

The presence of two different desorption temperatures observed following CO adsorption for the catalysts having the same surface state but different bulk compositions suggests that the observed CO₂ results both from CO oxidation and with oxygen from particles bulk and CO disproportionation. This is consistent with the TPD profile observed for the pre-oxidized catalyst, which clearly shows the presence of two desorption features both for CO and CO₂. The present TPD results show that CO adsorption on Pd-Ce/Al₂O₃ catalysts is not structure sensitive since we have obtained qualitatively similar results on three Pd-Ce/Al₂O₃ catalysts prepared by different methods, when subjected to the same pretreatment. Over oxidized and pre-reduced catalysts, the TPD spectra for the Pd/Al₂O₃ system are similar to those obtained for Pd-Ce/Al₂O₃ system. This suggests that there is no evidence of a Pd-Ce interaction affecting CO adsorption.
Unlike Pd/Al₂O₃ prepared by impregnation, the desorption profiles for ceria containing catalysts present many features over a large temperature range 373-1023K. The complexity of these spectra is due to the reactivity of both palladium and ceria for NO decomposition. Regarding the adsorption and reaction properties of Pd-Ce/Al₂O₃, the TPD results show that there are significant changes due to the presence of Ceria, mainly after reduction pretreatment.

When performed over an oxidized catalyst, NO desorption indicates the presence of reversibly adsorbed NO which can desorb from the surface in the low-temperature region (373-573K) as well as in the mid (573-723K) and high (723-923K) temperature regions. The three distinct features in the NO desorption profiles suggest that there are at least three types of sites available for NO adsorption. The presence of two types of adsorbed NO species over Pd-catalysts has been reported in the literature earlier [82-84] and these have been attributed to monomeric and dimeric NO adsorbed species. The high temperature feature (dimeric) has been proposed to be responsible for N₂O formation. Three species have also been observed previously [85,86] and have been attributed to linear and bridged NO species [87].

In our TPD experiments performed on oxidized Pd-Ce/Al₂O₃ catalysts, a distinct feature due to N₂O was observed which corresponds to the mid-temperature desorption feature of NO. This indicates clearly that, of the three types of NO adsorption sites, only the low temperature site cannot be associated with N₂O formation. Indeed, the first NO feature (NO weakly adsorbed) desorbs before the temperature of NO decomposition is reached. This explanation is based on the assumption that NO starts to decompose at the temperature at which N₂ starts to desorb in TPD [88]. Over a Pd/Al₂O₃ catalyst however, N₂O starts to desorb at 373K suggesting that the low-temperature NO site can be involved in N₂O formation as well as the two other sites. In addition, this result also indicates that the low-temperature NO peak, observed over all catalysts, cannot be attributed to a single NO species, the same for all catalysts. Moreover, our results show that, for all oxidized Pd catalysts, NO₂ formation is associated with the high temperature NO feature.

Significant differences were observed when TPD experiments were performed over pre-reduced catalysts. The pre-reduced Pd-Ce/Al₂O₃ system was observed to be more reactive than the pre-reduced Pd/Al₂O₃ system. In addition, the observed NO desorption profiles depended on the preparation method of the catalyst. The formation of N₂O is shown to be associated with a number of adsorption sites in the mid- and high-temperature regions. It is clear from these results that ceria considerably affects the properties of palladium for NO adsorption.

Our TPD results also show that the effect of reducing Pd-Ce/Al₂O₃ catalysts is to increase the fraction of NO which dissociates. However, the same reducing pretreatment decreases the fraction of NO which dissociates over Pd/Al₂O₃ system. Moreover, reduction favors the formation of N₂ over N₂O over Pd-Ce/Al₂O₃ catalysts. The results for NO suggest that reactions of this molecule will also be strongly affected by the presence ceria under reducing conditions.

The differences in the desorption features observed for the reduced catalysts prepared by different methods suggest that the active sites are located rather at the Pd-ceria boundary than on palladium and/or ceria particles. Our results indicate that controlling the preparation conditions, high N₂ selective catalysts could be obtained. This is the case for the reduced catalysts prepared by successive impregnation, which showed a high selectivity in a narrow temperature domain (between 573 and 773K). Because in both the TEM investigations and UV-Vis characterization the PdCeAl-co-impregnation and PdCe-successive impregnation looked similar (no Ce-Pd interaction was observed), but behaved very differently in the NO-TPD experiments, our results indicate that the NO dissociation site is most likely located at the palladium-ceria interface. Consequently, maximizing the boundary surface is expected to improve the N₂ selectivity.
these reasons, further investigations oriented toward the ceria particle size and phases distribution onto the support will provide useful information to optimize the performance of the catalyst.

References

CONTRIBUTIONS OF LATTICE OXYGEN IN METHANE COMBUSTION
OVER PdO - BASED CATALYSTS

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Abstract

Zirconia-supported Pd$^{16}$O and bulk Pd$^{16}$O were used as methane combustion catalysts for a reaction mixture containing 1% methane and 4% $^{18}$O$_2$ in helium. The methane oxidation reaction was performed in pulsed experiments and the distribution of oxygen isotopes among the reaction products was monitored. The $^{18}$O content of the catalyst following labeled reaction mixture pulses was determined by catalyst reduction with either diluted hydrogen or diluted methane pulses.

At low reaction temperature both CO$_2$ and water contained primarily $^{16}$O. As temperature increased, however, the $^{18}$O distribution in water and carbon dioxide changed differently. The isotopic composition of water molecules reflected the oxygen isotopic distribution in the bulk of the catalyst particles as determined by post reaction reduction experiments. The larger concentration of $^{18}$O in the carbon dioxide is explained by the differences in residence time and mobility of the products water and CO$_2$ on the catalyst. The hydrogen/water samples the bulk, while the CO$_2$ reflects the surface composition. The behavior of the zirconia supported catalyst was similar to the bulk PdO at the lowest temperature; however, as the temperature was increased above 600K, oxygen exchange with the support became important.

The catalyst behavior is explained by the presence of a single oxygen species at the catalyst surface: a bridge-bound oxygen to two palladium atoms. The surface is involved in the methane reaction mechanism by successive reduction/reoxidation cycles. Reoxidation uses both bulk and gas phase oxygen, and also oxygen from the support in the case of zirconia supported catalyst. Under these conditions the gas phase oxygen exchange with the catalyst is limited by the methane oxidation surface reaction.

Keywords: Palladium oxide, methane combustion, labeled oxygen, surface oxygen

Introduction

Palladium-based catalysts are largely accepted as the most effective catalytic systems for the methane combustion reaction. Despite extensive study at a wide range of reaction conditions, there is a lack of agreement concerning the methane oxidation reaction mechanism under fuel lean conditions over the oxide phase of the catalyst (i.e. in 473 – 923K temperature range).

Early pulsed reaction studies of Müller et al. [1] employed zirconia supported PdO catalysts labeled with Pd$^{18}$O, prepared from amorphous Pd – Zr alloys. These authors proposed that, both at 573K and 773K, the combustion reaction proceeds partly via a redox – Mars and van Krevelen – mechanism, but that the overall conversion is determined by the interplay between the surface reaction of “adsorbed” reactants and the redox mechanism. This study also reported an important influence of the oxygen isotopic exchange of carbon dioxide between the gas phase and the Pd$^{18}$O surface on the distribution of the carbon dioxide isotopomers, while the isotopic exchange of gas phase oxygen was negligible.

In a more recent paper [2] these authors concluded that the abstraction of hydrogen atoms from the adsorbed methane species is a “normal surface reaction”, whereas the formation of oxygen – carbon bonds is more controlled by a redox mechanism involving lattice oxygen.

Based on turnover rate measurements of the methane combustion reaction performed over zirconia-supported catalysts, Fujimoto [3] proposed a set of elementary steps describing the reaction mechanism. In the proposed mechanism, the catalytic site is considered as a surface
Appendix I

oxygen vacancy or coordinatively unsaturated Pd site on the surface of PdO crystallites, depicted generally by “Pd-PdO site pair”. In a later work [4] these authors concluded that the overall mechanism resembles Mars – van Krevelen reduction–oxidation pathways in which “carbon atoms in the gas phase or physisorbed CH₄ interacts with coordinatively unsaturated Pd sites on the surface of PdO crystallites and H atoms are abstracted sequentially from adsorbed CH₄ by neighboring Pd − O surface species to form surface hydroxyl groups (Pd − OH)” [4]. The authors claimed the proposed mechanism avoids the need for the coexistence of a separate Pd metal phase in atomic contact with PdOₓ during methane oxidation.

The mechanism proposed by Fujimoto [3,4] was further studied in the more recent work of Au-Yeung et al.[5]. They performed the methane combustion reaction over zirconia-supported Pd¹⁶O particles using continuous flow of a reaction mixture containing¹⁶O₂ and ¹⁸O₂ in equal amounts, in the 500–600 K temperature range. These authors observed negligible oxygen scrambling but important CO₂ scrambling during methane combustion. They also suggested that “lattice” oxygen is used more efficiently than oxygen from the gas phase in methane combustion.

None of the above mentioned studies [1 – 5] measured the distribution of oxygen isotopes in the water molecules produced in the methane combustion reaction in a systematic manner. In addition, the catalysts used in the previous studies [1 – 5] were all supported on zirconia carriers, a support with relatively high oxygen mobility at moderate and high temperatures [6]. Therefore oxygen can be exchanged between the PdO and the support and influence the distribution of oxygen atoms in the reaction products.

The purpose of this work was to study the behavior of unsupported and zirconia-supported PdO particles in the methane combustion reaction in the presence of ¹⁸O₂, measuring the ¹⁸O atoms distribution among the reaction products, including water.

Experimental

The catalysts employed in this study were pure PdO (99.999% of purity) provided by Aldrich, and zirconia supported PdO (3% wt. as Pd) obtained as described elsewhere [7]. The average PdO particle size of the fresh supported catalyst determined from XRD was 10nm [7]. The reaction mixtures used consisted of 1% methane, 4% oxygen and helium balance. The one containing regular ¹⁶O₂ was provided by Airgas, while the one labeled with ¹⁸O₂ (>97%) was obtained from Isotec.

The reactivity tests were performed in a fixed bed alumina tubular reactor with 4 mm internal diameter, placed in an electric furnace with automated temperature control. The reaction system allowed operation in two modes: continuous flow mode in which the reaction mixture continuously flowed through the catalytic bed, and pulse mode in which the reaction mixture was injected in a carrier (helium) stream that was flowing continuously over the catalyst. The reaction products were injected in a gas chromatograph equipped with methanizer and FID that allowed measurement of the CO, CO₂ and CH₄ concentrations in the reactor effluent stream. For the pulsed experiments, a capillary tube was placed downstream of the catalytic bed and was connected to a mass selective quadrupole detector HP 5971A. The capillary tube between the reactor and the mass spectrometer was heated to minimize adsorption of water molecules on the walls. This analytic system allowed determination of the distribution of oxygen atoms among the combustion reaction products: carbon dioxide (C¹⁶O₂, C¹⁶O¹⁸O and C¹⁸O₂) and water (H₂¹⁶O and H₂¹⁸O), respectively, as well as in the unreacted oxygen (¹⁶O₂, ¹⁶O¹⁸O and ¹⁸O₂).
The experimental runs with pure PdO employed 3 mg of catalyst sustained in the reactor on an alumina wool bed. Before each test, the catalyst was completely reduced with hydrogen and reoxidized under flowing oxygen overnight at 823K. After the oxidizing treatment, the catalyst was pretreated with several pulses of methane, after which it showed constant activity with a series of unlabeled reaction mixture pulses at 745K. A typical run consisted of two series of 17 labeled reaction mixture pulses (0.5 ml) injected over the fully oxidized and activated PdO at constant temperature, followed by reduction either with diluted hydrogen (5% H₂ in helium), or diluted methane (0.916% CH₄ in helium) pulses at the reaction temperature. This allowed measurement of the distribution of oxygen isotopes in the catalyst. The time interval between successive pulses in a series was 80 seconds. The time break between the pulse series was about 250 seconds. Complete reduction was achieved with continuous flow of hydrogen after each series of pulsed experiment.

For the tests with the zirconia-supported PdO, 9 mg of fresh catalyst were loaded in the reactor. Before and after the first test, the catalyst was cycled between room temperature (RT) and 1173K under continuous flow of regular reaction mixture at a heating/cooling rate of 5K/min in order to ensure a constant activity of the catalyst, as discussed elsewhere [7]. On cooling down, the ramp was stopped at 700K for the first test, or 600K for the second one, respectively, and the reaction system was switched to pulse mode. After the temperature stabilized, two series of 17 labeled reaction mixture pulses (0.5 ml) were injected at the same time interval as with unsupported particles, followed by a series of diluted methane pulses for catalyst reduction. Complete reduction of the catalyst was accomplished with continuous flow of diluted hydrogen for 30 minutes. The catalyst structure did not change significantly in a manner that affected reactivity after several of the cycles described. Runs at a fixed temperature repeated at the end of this study were virtually indistinguishable with those recorded initially. The sequences of runs are summarized in Table 1.

Because the catalyst is under flowing He (containing <1ppm of oxygen as stated in the manufacturer catalog) between pulses at temperatures below 750K, we checked whether the catalyst could become partially reduced at these conditions. To this end, a catalyst sample having a stabilized activity was held under flowing helium for 45 hours at 735K. Series of pulses were injected after 16, 23, 39 and 45 hours. The average methane conversion observed with reaction mixture pulses decreased from 84 to 80% after 16 hours, to 79% after 23 hours, to 71% after 39 hours and to 70% after 45 hours. This decrease is similar to that of similar aging under continuous reaction conditions and is therefore attributed to changes in catalyst surface area. Also, in the actual experiments total conversion did not change pulse to pulse even though the $^{18}$O distribution changed dramatically.

Pulses of different volumes (i.e. 1 ml, 0.5 ml, 0.021 ml) of reaction mixture injected over the catalysts at constant temperature showed a linear dependence between the methane conversion and the pulse volume, suggesting no diffusional limitations under pulsed conditions. Isotopic scrambling of oxygen atoms between reaction products and the catalyst surface does not influence the distribution of $^{18}$O atoms in the reaction products.

Results

The only reaction products detected following reaction mixture pulses were carbon dioxide and water. Oxygen, carbon dioxide and water isotopomers were monitored using the
mass selective detector. The relative distribution of $^{18}$O atoms in the same product was
determined using the mass spectrometry analysis, the carbon material balance and conversion
being determined from gas chromatographic analysis. Therefore, in the mass selective detector
samples were analyzed for ions with masses 18 and 20 for water, masses 32, 34 and 36 for
oxygen, and masses 44, 46 and 48 for carbon dioxide isotopomers.

The distribution of oxygen isotopomers for all investigated temperatures was similar to
the one depicted in Figure 1 and showed no significant oxygen scrambling between surface and
gas phase oxygen, in agreement with previous results [1, 2].

The distribution of carbon dioxide isotopomers was determined for each pulse of labeled
reaction mixture injected at different temperatures over the unsupported Pd$^{16}$O particles. Because
the profiles were very similar, only those obtained for the lowest and the highest temperatures of
the investigated temperature range are given in Figure 2, and the distribution of the carbon
dioxide isotopomers that resulted from the last pulse of the series for each investigated
temperature is shown in Figure 3. The conversion per pulse was a function of temperature only
and was constant with pulse number.

The first labeled reaction mixture pulse over Pd$^{16}$O catalyst produced predominantly
C$^{16}$O$_2$ at all investigated temperatures, suggesting lattice oxygen is predominantly used for
methane combustion. Except for the lowest temperature (600K), the relative fraction of C$^{16}$O$_2$
decreased rapidly with the number of pulses and then changed to a lower, constant slope,
maintained up to the end of the labeled reaction mixture pulse series. It should also be noted that
the longer break after pulse number 17 produced a slight increase in the C$^{16}$O$_2$ relative fraction.
This increase is rapidly lost and is due to an increase of surface $^{16}$O concentration caused by bulk
oxygen migration towards the surface. Conversion was constant for all pulses at a fixed
temperature even though the isotopic distribution changed markedly indicating a single
mechanism. The distribution of carbon dioxide isotopomers resulting from the last pulse injected
at different temperatures is shown in Figure 3. As temperature increases, the amount of $^{18}$O in
the carbon dioxide increases steeply with a much slower increase at higher temperatures, typical
of a transport limited process. This suggests that labeled oxygen uptake is limited by exchange
with the bulk.

Figure 4 shows the relative distribution of the water isotopomers for three temperatures
(a), and as observed for the water produced with the last pulse of the series at different
temperatures (b). As expected, the concentration of H$_2^{18}$O increased as the pulse number
increased and as temperature increased. The isotopic composition of water resulting from
methane combustion over Pd$^{16}$O catalyst showed a higher initial concentration of $^{16}$O-containing
species, followed by a much smaller decrease as the pulse number increased, compared to CO$_2$.

In order to determine both the overall oxygen exchange and to qualitatively assess the
distribution of oxygen isotopes with the depth from the particle surface toward the bulk, the
catalyst was reduced after reaction at the reaction temperature using either diluted methane or
diluted hydrogen. The relative fractions of water isotopomers resulting from catalyst reduction at
different temperatures are given in Figure 5. Examining the plots in Figure 5 there are several
notable observations. First, as the temperature increases the uptake of gas phase oxygen onto the
catalyst increases. This is consistent with the increase in $^{18}$O-containing isotopomers in CO$_2$ and
the increase of the H$_2^{18}$O concentration in reaction products with the reaction temperature.
Another interesting observation is that, assuming a “layer by layer” reduction mechanism both
for reduction with methane and hydrogen pulses, the $^{18}$O concentration gradient between bulk
and surface is small and increases slightly with the temperature, suggesting that $^{18}$O exchanged
becomes limited by penetration of $^{18}$O into the bulk. A final interesting observation is that the distribution of water isotopomers produced during the reaction is similar to the one observed in reduction experiments, suggesting the composition of water resulting from the reaction reflects the bulk composition of the catalyst particle. For reduction with diluted methane (665K and 745K), the conversion resulting for the first reducing pulse equaled the one observed with the last reaction mixture pulse. When hydrogen was used as reductant, because of its high reactivity for PdO reduction we assumed total conversion, consistent with the equal number of hydrogen pulses consumed to reduce the catalyst after reaction at different temperatures (600K, 625K, 670K and 700K). For the above reasons Figure 5 is presented as distribution of isotopomers versus percent of the catalyst reduced.

The zirconia-supported catalyst behaved similarly at the lowest temperature of these experiments. However, the distribution of carbon dioxide isotopomers plotted in Figure 6 for two temperatures shows significant differences. The most important feature is that at higher temperatures the amount of $^{16}$O in the reaction products is considerably higher for similar amounts of methane converted. This suggests an important contribution of the support to the $^{16}$O pool of the PdO phase. The increase of the $^{16}$O content in the reaction products as the reaction temperature increases is most likely due to an increase in the oxygen exchange rate between the PdO particles and the zirconia support and follows the temperature dependence observed by Duprez et al. [6] for oxygen mobility on zirconia.

The important contribution of the support to the oxygen pool of the catalyst is also suggested by the distribution of water isotopomers depicted in Figure 7. Again, the $^{18}$O-containing isotopomer is more abundant at lower temperature, suggesting a more rapid depletion of $^{16}$O at lower temperature and a lower rate of oxygen exchange between support and PdO particles.

The isotopic distribution for carbon dioxide and water resulting from reduction experiments performed with diluted methane are given in Figures 8 and 9, respectively. At 600K the first reduction pulse gave $^{18}$O-rich reaction products suggesting the PdO surface is rich in $^{18}$O. As the PdO phase is depleted of oxygen during the reduction, $^{16}$O from the bulk becomes accessible. By contrast, at 700K the oxygen exchange rate between support and PdO particles is fast so that the oxygen isotopes at the surface are equilibrated with the support (having a large reservoir of $^{16}$O). The $^{18}$O exchange from the gas is much slower than the exchange from the support, so that the bulk and surface are also equilibrated. Note that the PdO particle size is much smaller than the grain size in the pure PdO catalysts, which affects the equilibration time. Therefore, for all the reduction pulses at the higher temperature of 700K the isotopic composition of the reaction products changes insignificantly.

**Discussion**

Our main goal was to investigate and understand the physical and chemical processes determining the surface reduction and reoxidation during methane combustion at the PdO surface. The pulsed reaction technique was used because it allows study of the evolution of the surface of the catalyst at a low number of turnover cycles. This can be accomplished by injecting small amounts of reaction mixture over a large amount of catalyst.

The distribution of CO$_2$ isotopomers obtained in our experiments is apparently different from that reported by Muller and co-workers from similar experiments [1]. In fact our catalyst
responded similarly. The reason for the apparent difference is that, working at very high conversions per pulse, the number of turnover cycles performed during one pulse in Muller's study is significantly higher than in our work, thus the analysis of the final reaction product reflects, in fact, the average of a large number of turnovers. Moreover, because of the longer contact time, readesorption of the reaction products is important in their experiments; therefore isotopic scrambling affects the final distribution of oxygen isotopes in the reaction products. In our work the number of turnovers averaged in a single pulse is considerably lower, thus allowing a stepwise observation of the oxygen isotopes' distribution among the reaction products without a significant effect of isotopic scrambling of oxygen atoms between the PdO surface and gas phase molecules.

From the point of view of the reaction mechanism, Fujimoto et al. [3, 4] proposed a set of elementary steps in which the catalytic site is an oxygen vacancy or coordinatively unsaturated Pd site on the surface of PdO crystallites. They concluded that the mechanism resembles the Mars and van Krevelen mechanism and avoids the need for the coexistence of a separate Pd metal phase in atomic contact with PdOx during methane oxidation [4]. A possible methane activation step is the dissociative adsorption of methane on a surface Pd – O pair as proposed by Broclawik et al. [8]. It should be noted that the reaction order with respect to oxygen reported by many investigators is positive and near zero. Vacancy development, especially under conditions where water is desorbed between pulses (pulsed experiments above 725K), would be expected to be negative order with respect to oxygen. Au-Yeung et al. [5] used an isotopically labeled technique to investigate the methane oxidation pathways on PdO catalysts. They concluded the lattice 16O in PdO is more efficiently used in methane combustion than labeled 18O atoms from the gas phase. Their results suggested reoxidation is slow and from an estimated 16O balance, either the bulk and surface are partially reduced, or oxygen exchange with the zirconia is fast. Based on results obtained with pulsed studies over zirconia-supported Pd18O catalysts prepared by oxidation of palladium-zirconia alloys, Muller and co-workers [2] concluded that the combustion reaction proceeds partly via a redox mechanism in which the abstraction of hydrogen atoms from the adsorbed methane species is a "normal surface reaction", whereas the formation of oxygen–carbon bonds is controlled by a redox mechanism. Their assumption was based on the differences observed between the distribution of labeled oxygen atoms in water and carbon dioxide products. However, these authors have not systematically monitored the water isotopomer distribution.

For an easier evaluation of the distribution of 18O in water and carbon dioxide isotopomers we introduce the gas phase oxygen distribution factor (ODF). For water, the ODF equals the relative fraction of H2 18O and for CO2 it is computed with the equation:

\[
(ODF)_{CO_2} = \frac{A_{48} + 2A_{46}}{2(A_{46} + A_{46} + A_{48})}
\]

In Figure 10 the values for the \((ODF)_{CO_2}\) are presented together with the lattice oxygen consumption (computed from the material balance) as functions of the reaction temperature. Comparing the \((ODF)_{CO_2}\) values with the similar \(H_2^{18}O\) profile depicted in Figure 4(b) one can easily observe the differences in the distribution of \(^{18}O\) in water and carbon dioxide following labeled reaction mixture pulses. However, during reduction with diluted methane pulses after reaction, an even distribution of \(^{18}O\) between water and CO2 was obtained, as plotted in Figure 11. Based on this observation one could be tempted to claim hydrogen and carbon are oxidized following different mechanisms.
The existence of different reaction mechanisms for the oxidation of carbon and hydrogen, respectively, would require the existence of two different types of oxygen at the catalyst surface. The crystal structure of PdO is a useful starting point in considering the types of sites that could be available for reaction on a PdO catalyst surface. Palladium oxide crystallizes in a tetragonal structure with lattice constants \(a = b = 0.305\) \(\text{nm}\) and \(c = 0.534\) \(\text{nm}\) at room temperature; Pd atoms are located at (0, 0, 0) and (0.5, 0.5, 0.5), and oxygen atoms at (0.5, 0, 0.25) and (0.5, 0, 0.75). As shown in the model in Figure 12(a), each Pd atom is coordinated to four O atoms in a square planar configuration while each O atom is surrounded by four Pd atoms in a tetrahedral pattern. Cleaving the structure perpendicular to [001] and [110] results in the least corrugated surfaces, and thus (001) and (110) surfaces are expected to be favored; models of the bulk-terminated surfaces are shown in Figure 12(b) and (c). In considering the surface models, a couple of points become immediately obvious. First, both surfaces expose only a single type of oxygen species: an oxygen atom bridge bound to two Pd atoms. Although much has been made in the literature about potential differences between "lattice" and "adsorbed" oxygen species, considering these models, it is difficult to envision an oxygen species in a site other than the bridge site. It should also be noted that the (100) and (010) surfaces also expose only a single type of oxygen species. The second point is that both surfaces are polar and thus must reconstruct to maintain charge neutrality. There has been no work reported on the surface structure of PdO, however, other oxides and binary compounds (such as halides [9] and III-V semiconductors [10]) maintain charge neutrality through ordered vacancy structures. Along these lines, removing half the surface oxygens from the bulk terminated PdO (001) and (110) surfaces would create charge compensated surfaces. Although this creates arrays of oxygen vacancies, the surfaces are fully oxidized in that all the surface Pd atoms are formally in a 2+ oxidation state. As a result, oxygen cannot adsorb at the vacancies without oxidizing the surface Pd atoms beyond the 2+ oxidation state. Considering that CH\(_4\) combustion is typically carried out under conditions that are near the thermodynamic border between Pd and PdO, adsorption on these vacancy sites under reaction conditions seems unlikely. Along the same lines, oxygen desorption from the charge compensated surface would require reduction of surface Pd atoms; oxygen desorption would then reoxidize the Pd atoms to Pd\(^{2+}\). While more massive reconstruction cannot be ruled out and defects such as steps and crystallite edges can create additional types of sites, the bulk crystal structure suggests only a single potential site for surface oxygen. If the edges and defects controlled reactivity, the reaction would be structure sensitive with small particles showing higher reactivity. This is not the case experimentally as particles less than 10 nm have been observed to show lower reactivity.

Although a single oxygen is likely responsible for reactivity at the conditions of our experiments, these results do not rule out the possible role of mixed phases under some reaction conditions. The experimental results presented here, however, indicate that oxygen migration in bulk PdO can be fast compared to reoxidation from the gas at low temperatures. Studies of the oxidation of metallic Pd indicate that the reaction can be slow [2, 5]. The above arguments suggest that Pd and PdO can coexist for extended periods at certain temperatures and oxygen pressures, which is not thermodynamically possible if equilibration with the gas phase is rapid. We also have shown that during methane oxidation reaction, surface reoxidation/oxygen exchange with the gas phase is slow. Figure 5 shows low \(^{18}\text{O}\) uptake, especially at low temperatures, and Figure 10(b) shows from the oxygen balance that at low temperature the exchange is limited by the surface reaction. In earlier work using high resolution transmission electron microscopy (HRTEM) we observed that in transient conditions the surface can likely
Appendix I

consist of a patchy array of phases; it is also consistent with previous TPD and STM results of Zheng and Altman [11] that indicate a sequence of four phases during Pd oxidation, confirming at least one stable intermediate state. Along these lines, at any point in time the condensed phases can be described by oxygen – palladium mole fractions. Since both the miscibility of oxygen in Pd and the oxygen deficiency of PdO are limited, separation of the Pd and PdO phases will occur. The mixed Pd-O surface would exist at the interface between the two bulk phases. The phase with the lowest surface tension would tend to completely encapsulate the higher surface tension phase. Since oxides typically have lower surface tension than metals, reduced Pd clusters formed during the reaction of methane with lattice oxygen at the PdO surface are likely to be encapsulated by the bulk oxide phase. The encapsulation mechanism likely consists of bulk oxygen diffusion towards the surface, thus in equilibration of the concentration of the vacancies between surface and bulk. This is consistent with our experimental observation that, at certain operating conditions, oxygen equilibration between the condensed phases can be fast compared to equilibration with the gas phase. Hence, Pd and PdO may coexist for an extended duration, even at high temperatures. These factors may affect reactivity when the catalyst is reduced and then exposed to reaction mixture.

Since reactivity did not change pulse to pulse at a fixed temperature even when the isotopic distribution changed dramatically, only a single oxidation mechanism is likely for the conditions of our study. This is consistent with a Mars and Van Krevelen reaction mechanism and only a single type of surface oxygen as discussed above. The difference in the distribution of $^{18}$O atoms between water and CO$_2$ cannot arise from differences in the reaction mechanism, or from oxidation using different type of surface oxygen species. The starting point in explaining this behavior is to identify the processes determining the isotopic composition of the PdO surface.

The reaction products resulted for all pulses contain $^{16}$O atoms, thus not only surface oxygen can participate in methane combustion, but also bulk lattice oxygen. Initially, the surface is totally $^{16}$O; therefore the first reaction mixture pulse is predominantly oxidized with $^{16}$O, which is reflected in the high concentration of $^{16}$O-containing reaction products observed for the first labeled pulse, independently on the reaction temperature. The reduced sites generated at the PdO surface following desorption of the reaction products are reoxidized either with labeled oxygen from the gas phase by dissociative adsorption, or with bulk $^{16}$O.

It should be noted here that the $^{16}$O/$^{18}$O ratio at the catalyst surface is determined by the ratio between the rates of the two reoxidation processes. Reoxidation from the gas phase is an activated process [12] and, thus, expected to be governed by an Arrhenius-type equation. The bulk oxygen diffusion is a mass transfer process. The activation energy for the oxidation is higher than for the diffusion coefficient. Consequently, the rates of the two concurrent processes are expected to respond differently with respect to temperature changes. At low temperatures, the oxygen uptake is limited by the methane oxidation reaction on the surface; as temperature is increased above 600K, bulk diffusion limits oxygen exchange. Indeed, the lattice oxygen consumption, which indirectly reflects the rate of bulk oxygen diffusion, has a stronger influence at lower temperatures as observed in Figure 10(b). The uptake of gas phase oxygen also meets the expected evolution. The post-reaction reduction experiments showed a small increase in the $^{18}$O uptake at low temperatures and a step increase between 700 and 745K.

Examining the driving forces of the two proposed reoxidation processes, it is clear that both are favored by high temperatures and high density of surface reduced sites. These two variables are inter-related and connected to the rate of reaction. Therefore, the dynamics of
oxygen atoms, both at the surface and in the bulk, is determined by the relative rates of these three processes: (i) reaction of methane at the catalyst surface, (ii) reoxidation of the surface with bulk oxygen and (iii) reoxidation from the gas phase. However, in balancing the contribution of each process to the overall kinetics, one should also take into account the general context determined by the pulse reaction technique, that is the surface is exposed to the reaction environment only for a limited time, and the processes taking place at low rates may not be equilibrated under these circumstances.

The low rate of water desorption at low temperature may cause a delay in the reoxidation from the gas phase. Due to the high concentration of surface oxygen vacancies resulting after water desorption during the time between reaction mixture pulses the surface is reoxidized with bulk oxygen; this process may take place continuously during the 80 seconds time interval between two successive pulses. This is reflected in the low concentration of $^{18}$O containing isotopomers observed during reaction at 600K. In support of this interpretation is also the increase in $^{16}$O concentration in the reaction products observed at all investigated temperatures following a longer 5 minute pause after the seventeenth pulse (see Figure 2) when the catalyst is exposed only to He (O$_2<1$ppm).

The hydroxyls produced by reaction have a long residence time on the catalyst at temperatures below 725K [13] and the hydrogen effectively samples the bulk. The isotopic oxygen distribution in water reflects that of the bulk (from reduction). By contrast, the CO$_2$ molecules do not sample the bulk and are quickly desorbed, thus reflecting an isotopic composition closer to the instantaneous composition of the surface in presence of gas phase oxygen. Therefore, a first important conclusion would be that, at low temperature, water desorbs from the surface after the partial pressure of oxygen above the catalyst decreased significantly, leading to the low uptake of labeled oxygen at 600K. This is consistent with our previously reported results [13] showing that water desorption lags significantly the carbon dioxide desorption. At temperatures above 600K, however, surface oxygen exchange becomes faster than exchange with the bulk and gradients develop in the particle. At 745K a step change in oxygen uptake is noted coincident with the temperature at which water is desorbed, on the same time scale as CO$_2$. Throughout the lower temperature range the oxygen exchange rate mirrors that of the methane oxidation reaction suggesting that the reaction provides sites for oxygen readsorption on a time scale faster than hydroxyl desorption. This is consistent with our finding at these temperatures and pulse conditions that CO$_2$ desorption significantly precedes water.

Along these lines, the reaction mechanism consistent with the experimental results presented here could be summarized in the following successive steps: (i) the methane molecule is activated possibly through reaction with a surface Pd-O pair following the mechanism proposed by Broclawik [8] with formation of a methyl fragment bound to the Pd$^{2+}$ ion and a hydroxyl group; (ii) the methyl fragment is further rapidly oxidized to CO$_2$ generating more surface hydroxyls; (iii) the CO$_2$ is rapidly desorbed generating a surface vacancy; (iv) if the oxygen partial pressure above the catalyst is high enough, the oxygen vacancy will adsorb oxygen from the gas phase, otherwise it will be filled with oxygen from the bulk; (v) following recombination of hydroxyls generated during methane oxidation, more surface oxygen vacancies are generated; they are partially filled with oxygen from the gas phase and partially equilibrate with the bulk; (vi) between pulses the oxygen on the surface exchanges with the bulk, therefore $^{18}$O from the gas phase migrates into the subsurface layers. At low temperatures this process is equilibrated; however, at higher temperatures a gradient develops between the surface and bulk.
The experimental results obtained with the supported catalyst indicate that zirconia is involved actively in the oxygen dynamics at the catalyst surface. However, at low temperatures (<600K) the oxygen exchange between the PdO phase and the support is slow.

During reduction with methane at 700K the oxygen transfer from the support to reoxidize the PdO particles causes the reduction of the support. Under reaction conditions that favor higher rates of oxygen exchange between PdO and support than the rate of bulk oxygen diffusion or the rate of oxygen exchange with the gas phase, the isotopic composition of the CO2 product would be determined by the oxygen exchange between support and the PdO phase. This may explain the behavior observed by Au-Yeung et al. [5] with their zirconia supported catalyst.

Studying both supported and unsupported PdO catalyst showed that the reaction mechanism is not influenced by the support. However, it significantly contributes to the oxygen pool of the catalyst. This explains the good results for ceria-zirconia as supports for combustion catalyst and supports the idea of a stabilizing effect for the PdO phase, as observed earlier [7].

Conclusion

We used isotopically labeled reaction mixture pulsed experiments with pure and supported Pd16O particles in order to investigate the contribution of the lattice oxygen in the reaction mechanism of methane combustion. Several conclusions derived from the results presented here.

- Although much has been made in the literature about potential differences between lattice and adsorbed oxygen species at the PdO surface, based on thermodynamic considerations we showed that the most favorable surfaces (001) and (110) expose a single type of oxygen species: an oxygen atom bridge bound to two Pd atoms. At our experimental conditions the reactivity data shows that this one form of oxygen is responsible for the oxidation of the carbon and hydrogen in the methane.

- The differences in the labeled oxygen atoms distribution between water and carbon dioxide are not due to different oxidation mechanisms for hydrogen and carbon, respectively, as it was previously suggested in other studies [1]. Our results clearly indicate that, because of a lower rate of water desorption relative to the rate of isotopic equilibration of surface and bulk oxygen, and because hydrogen samples the bulk, the water molecules produced in the combustion reaction reflect the composition of the bulk catalyst. Carbon dioxide is desorbed more rapidly and it is reflective of the isotopic composition of the surface.

- Surface hydroxyls resulting from methane dissociation at the PdO surface impede the oxygen uptake by the catalyst. In pulsed experiments performed at temperatures below 745K, because of the longer residence time of hydroxyl groups at the surface, following water desorption the oxygen partial pressure in the gas phase is too low to allow a significant oxygen uptake onto the reduced surface. As temperature increases, the rate of water desorption increases significantly, as well as the oxygen uptake. Therefore, the inhibitory effect of water molecules on the activity of the PdO catalyst for methane combustion can be explained, at least partially, by the mechanism discussed above.

- The zirconia support contributes significantly to the oxygen pool of the PdO phase available for the methane combustion. Experiments performed with isotopically labeled
reaction mixture at two temperatures showed that at 700K the exchange of oxygen between support and PdO is very rapid.

Acknowledgements

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References

### Table 1. Sequences of experimental runs

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M/a – catalyst activation with methane pulses; A/c – activity check with reaction mixture pulses (CH₄:¹⁶O₂:He = 1:4:95); LRM/p – labeled reaction mixture pulses (CH₄:¹⁶O₂:He = 1:4:95); H/p – reduction with 5% H₂ in He pulses; o/n O – treatment under flowing ¹⁶O₂ overnight; DM/p – diluted methane (0.916% of methane in He) pulses for catalyst reduction; Total reduction was performed with continuous flow of 5% of hydrogen in He for 30 minutes at the test temperature. Cycling was performed at 5K/min heating/cooling rate under flowing of unlabeled reaction mixture. The values in square brackets are the temperatures for each sequence.
Appendix I

Figure captions

Fig. 1. Typical distribution of oxygen isotopomers following labeled reaction mixture pulses over unsupported Pd^{16}O particles.

Fig. 2. Distribution of the carbon dioxide isotopomers observed with labeled reaction mixture pulses injected over the unsupported Pd^{16}O particles at 600K and 745K.

Fig. 3. Distribution of the carbon dioxide isotopomers resulted for the last pulse of the second series of labeled reaction mixture pulses injected over unsupported Pd^{16}O particles at different temperatures.

Fig. 4. Distribution of water isotopomers observed for labeled reaction mixture pulses injected over unsupported Pd^{16}O particles at different temperatures (a) and the relative fractions of H_2^{18}O determined for the last reaction mixture pulse at the reaction temperatures used (b).

Fig. 5. Distribution of water isotopomers at different stages of PdO reduction using hydrogen (600 and 700K) or methane (665 and 745K). Reduction performed at the same temperature as the reaction.

Fig. 6. Carbon dioxide isotopomers distribution resulted following labeled reaction mixture pulses injected over zirconia supported Pd^{16}O particles at 600 and 700K.

Fig. 7. Distribution of water isotopomers observed following labeled reaction mixture pulses over zirconia supported Pd^{16}O particles at different reaction temperatures.

Fig. 8. Carbon dioxide isotopomers distribution observed during the reduction of the zirconia-supported catalyst with diluted methane pulses after labeled reaction mixture pulses at 700K (a) and 600K (b).

Fig. 9. Distribution of water isotopomers during the reduction of the supported catalyst using diluted methane pulses after labeled reaction mixture pulses injected at different temperatures.

Fig. 10. The ODF values for carbon dioxide (a) and the overall lattice oxygen consumption (b) at different reaction temperatures.

Fig. 11. The ODF values for water and carbon dioxide determined for the reduction of unsupported catalyst with diluted methane pulses.

Fig. 12. Crystalline structure of PdO: (a) unit cell; (b) and (c) bulk terminated (001) and (110) surfaces, respectively;
Fig. 1
Fig. 2
Fig. 3
Fig. 4

Test temperature:
600K 665K 700K

Relative fractions

Pulse number

Reaction temperature, K

Relative fraction of H\textsubscript{2}\textsuperscript{16}O

Relative fraction of H\textsubscript{2}\textsuperscript{18}O
Fig. 5

Relative fractions

\[ \text{H}_2^{\text{16}} \text{O}, \text{H}_2^{\text{18}} \text{O} \]

- reduced with H\(_2\) at 600 K
- reduced with CH\(_4\) at 665 K
- reduced with H\(_2\) at 700 K
- reduced with CH\(_4\) at 745 K

% of reduced catalyst
Fig. 6

Pulse number

Relative fractions

600K

700K

$C^{16}O_2$

$C^{16}O^{18}O$

$C^{18}O_2$
Fig. 8

600K

700K

Pulse number

Relative fractions
Reaction temperature:
600K 700K

Relative fractions

$H_2^{16}O$

$H_2^{18}O$

Fig. 9
Fig. 10

(a) Oxygen from total in catalyst, %

(b) Total $^{16}$O in reaction products, mol x $10^6$
- $^{16}$O consumed
- $^{18}$O after reaction

Reaction temperature, K

Legend:
- This study
- Muller et al. [1, 2]
- Au-Yeung et al. [5]
Reduction temperature:
665K  745K

\( (ODF)_{H_2O} \)
\( (ODF)_{CO_2} \)

Fig. 11

Pulse number
TEMPERATURE AND TIME DEPENDENCE OF THE WATER INHIBITION EFFECT ON SUPPORTED PALLADIUM CATALYST FOR METHANE COMBUSTION

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Abstract
The time constant for equilibration of water adsorption/desorption during methane combustion over zirconia supported palladium catalyst was qualitatively studied at different reaction temperatures under both pulsed and continuous flow experiments. Water inhibition of methane oxidation was found to depend strongly on the time constant for equilibration of the adsorption/desorption of water, which, in turn, is a strong function of temperature. In pulsed experiments, at temperatures below 723K, the water inhibition effect was found to be important, in agreement with previously reported results and consistent with results reported by other authors. This also coincides with the temperature at which desorption time gap between the measured CO₂ and water peaks disappears. Response to changes in water concentration was found to be slow, thus not equilibrated at low temperatures. However, under continuous flow water poisoning is important to higher temperatures due to readsoption.

Keywords: Palladium oxide, catalytic combustion, water inhibition.

Introduction
The inhibition effect of water molecules on the performance of palladium catalysts for methane combustion is widely accepted. Several studies [1 - 6] have presented evidence of this phenomenon at reaction conditions where PdO is known to be the thermodynamically stable phase of the catalyst. However, the kinetics of water desorption from the catalyst surface, as part of the overall kinetics of methane combustion, remains a matter of debate. There is a lack of agreement on the reaction order with respect to water and on the effect of temperature on the inhibition phenomenon.

Early work of Cullis and Willatt [1] reported no effect of water at concentration levels resulting from the methane combustion reaction (pulses of a stoichiometric mixture of methane and oxygen). Constant reaction orders with respect to water of −0.98 and −0.8 ± 0.2 were reported by Ribeiro [2] and van Giezen [3], respectively, in continuous flow reaction experiments performed at 550K and 353 – 788K, respectively. However, Burch et al. [4, 5] suggested the water inhibition effect is temperature dependent. They observed that the presence of water in the reaction mixture pulses injected at intervals of 2 – 3 minutes over an alumina supported PdO catalyst does not affect its activity at temperatures above 723K.

In a recent study [6] we observed higher apparent activation energies for the combustion reaction at lower temperature/conversion region. Similar observations were reported by Carstens et al. [7] and Ahlstrom-Silversand and co-workers [8]. We proposed two reasons to explain this

*Corresponding author
behavior: (i) the reaction order with respect to water is temperature dependent, and (ii) there is a long time required for the equilibration of surface water concentration in response to changes in the gas phase water concentration.

In the present work we bring new experimental evidence to support the previously proposed explanation [6]. We directly demonstrate how the time factor affects the water inhibition effect on the PdO phase of the catalyst and its dependence on the reaction temperature.

Experimental

The catalyst was prepared by wet impregnation of a palladium nitrate solution from Aldrich on a zirconia support prepared using zirconyl nitrate hydrate from Aldrich as precursor, following a procedure described elsewhere [9]. After impregnation, the catalyst was calcined for 2 hours at 873K in flowing oxygen. The palladium content of the catalyst was 3% with an average particle size of 10 nm as determined from XRD analysis [6].

Approximately 50 mg of fresh catalyst was loaded into an alumina tubular reactor with 4 mm internal diameter. The reactor was placed in an electric heater equipped with automatic temperature controller. The experimental setup allows the reactor to be operated both in continuous reaction mixture flow mode, and in pulse mode. The pulse mode consists of 20 μl reaction mixture pulses injected in the helium carrier stream that continuously flows through the catalytic bed. The switch from one mode to another can be accomplished on a minute time scale.

The contact time both for pulsed and continuous flow experiments is below 0.5s. For the continuous flow experiments, a linear dependency was found between the methane conversion and the reaction mixture flow rate at different constant temperatures in the range of those used in our experiments. These results suggest that there are no transport limitations for these reaction conditions.

The reaction mixture used for the wet feed experimental runs was saturated with water vapor in a temperature controlled saturator. The water concentration used in a typical run with "wet" feed was 2%, both for continuous flow or pulsed experiments.

Before each experiment the catalyst was cycled under a continuous reaction mixture flow (CH₄:O₂:He = 1:4:95 from Airgas) between room temperature and 1173K, at a 5K min⁻¹ heating/cooling rate. According to our previous experience [6], this treatment enables the catalyst to preserve a constant activity vs. time on stream for more than 24 hours.

Reaction products were analyzed with a gas chromatograph equipped with methanizer and FID. This analytic setup allows determining the carbon oxides (CO and CO₂) and the unreacted methane concentrations in the reactor effluent. Gas samples were also taken from the reactor immediately downstream of the catalytic bed and directed through a capillary pipe to a quadrupole mass spectrometer. The capillary tubes between reactor and the mass selective detector were heated in order to minimize water adsorption on the walls. This complementary analytic system allowed determination of the relative desorption rates of the reaction products.

Results

For the first set of experiments the catalyst was heated under flowing helium at different temperatures. After the temperature stabilized at the desired value, a series of 16 dry reaction mixture pulses were injected at a constant time interval of 80 seconds. The methane conversion did not change with the number of pulses at constant temperature (T>600K), being only a function of temperature. After a pulse series at constant temperature, the catalyst was further
heated under flowing helium to the next desired temperature in a time scale of tens of minutes (usually 30 to 40 minutes) and the pulse series resumed.

The mass spectrometry analysis showed the expected stoichiometric distribution of the reaction products at constant temperature, except for the first two pulses when the water peaks were weaker, suggesting some of the water remained adsorbed in the system. The peak maxima observed with the mass spectrometer for methane, carbon dioxide and oxygen occurred with the same temporal profile, the maximum signal corresponding to the water peak, however, was delayed. For comparison purposes, in Table 1 temporal profiles for methane, water and carbon dioxide as resulted at three different temperatures are shown. The extent of the delay in the water peak maximum changed with the reaction temperature as depicted with solid squares in Fig. 1.

The constant delay observed at high reaction temperature is most likely caused by water adsorption on the capillary pipe between reactor and the mass spectrometer. At low reaction temperatures this effect is combined with a slower rate of water desorption from the catalyst surface, which leads to larger delays in the water peak maxima.

A similar experiment was performed replacing the reaction mixture pulses with pulses of 1% oxygen in helium containing 3.45% water. The composition of the reactor effluent was monitored for oxygen and water with the mass spectrometer. Again the water peaks were delayed compared to the oxygen peaks, but the time gap between the peaks was smaller than that observed under reaction conditions at the same low temperatures, and became constant for temperatures above 550K (see open squares in Fig. 1) suggesting a slow adsorption of water from the gas phase at the catalyst surface.

The next experiments were performed in a dynamic temperature regime heating up at 5K/min. The temperature programmed reaction profiles for methane oxidation were recorded under both continuous flow (circles in Fig. 2) and pulsed flow (squares in Fig. 2) modes. During the pulsed TPR profile, “dry” or “wet” reaction mixture pulses were injected in the helium stream each 3 minutes. Between consecutive pulses the catalyst was held under flowing helium.

Under continuous flow of reaction mixture the TPR profiles obtained for “dry” and “wet” feeds are parallel for the investigated temperature range, consistent with our previously reported results [6] obtained with continuous flow of “dry” and “wet” reaction mixture between 623K and 1173K where the PdO phase of the catalyst is stable under the reaction conditions. By contrast, with reaction mixture pulses, the methane conversion obtained with “wet” feed reached the value observed with “dry” feed at about 773K, suggesting no water inhibition effect at that temperature. It could also suggest that the inhibition becomes saturated at a given water concentration, but this would be inconsistent with the trend noted for the continuous flow data. In addition, the activity in pulsed mode is considerably higher than in continuous mode.

It should also be noted that the conversion observed for the first “wet” pulse injected (open square symbol numbered 1 in Fig. 2) is located on the “dry” feed TPR profile. This feature was not an artifact being completely reproducible after a second heating/cooling cycle between 573 and 773K in helium flow, confirming the slow uptake of water by the catalyst at low temperatures.

Finally, a last pulsed experiment was carried out with “dry” and “wet” reaction mixture pulses injected over the catalyst at a constant temperature of 573K. This temperature is shown because the inhibition effect is strong (approximate reaction order with respect to water of -1) at this low temperature. The time interval between consecutive pulses was held constant at 5 minutes. The methane conversion recorded for consecutive pulses are depicted in Fig. 3. The conversion decreased with the number of pulses for the “wet” reaction mixture. Importantly, the
methane conversion recorded for the first “dry” and “wet” pulses were approximately equal. After the third pulse, the conversion observed with “wet” feed leveled off to a constant value, lower than the corresponding “dry” pulses. These observations are consistent with water equilibration occurring on the several minute time scale at 573K. A similar experiment performed at 523K with dry feed at the same time interval between successive pulses showed a decrease of methane conversion from 10.4% to 6.8% for the first 7 – 8 pulses followed by constant activity for the next 10 pulses.

Discussion

Cartens et al. [7] reported higher apparent activation energies for the low temperature/conversion region for methane oxidation over a Pd/ZrO₂ catalyst. They observed two distinct branches of the Arrhenius plot: below 465K the apparent activation energy was found to be 42.8 kcal/mole, while above this temperature, it was 20.8 kcal/mole. These values were determined without correcting for water poisoning. In the transient region between the two regions characterized by different apparent activation energies, the apparent activation energy measured was a function of the heating rate, suggesting a strong time-dependent component with the kinetics of the process. One could be tempted to assign this behavior to the activation of the catalyst as the temperature increases, consistent with results reported in many studies [1, 6, 10, 11]. However, the same behavior was reported by Alkstrom-Silversand [8] with Si-stabilized alumina-supported palladium catalysts on cooling down the reaction temperature after the catalyst had been “activated” on a heat up cycle. We obtained superimposable Arrhenius plots on heating and cooling the temperature of the catalyst at a constant 5K/min rate [6]. These results clearly showed that the differences between the apparent activation energies for low and high temperature/conversion regions of the Arrhenius plots are not caused by catalyst activation.

In previous kinetics studies, the reaction order with respect to water was determined assuming no temperature or time effect for water equilibration. For example, Ribeiro et al. [2] found – 0.98 reaction order with respect to water, but this value was determined from data recorded at 550K constant temperature. Van Giezen [5] found constant – 0.8 ± 0.2 order with respect to water for continuous flow of “wet” reaction mixture in 353 – 788K temperature range. To determine this value the author assumed zero order reaction orders with respect to oxygen and CO₂, and constant reaction orders with respect to methane and water for the investigated temperature domain. They also assumed constant activity vs. time on stream, and that the catalyst responds immediately to changes in water concentration on both heating and cooling ramps. However, we showed that the reaction order with respect to water changes with the temperature and methane conversion (water concentration) [6]. Moreover, the equation proposed by van Giezen \[ \left( E_A \right)_{app \, dry} = \frac{1}{(1 - \gamma)} \left( E_A \right)_{app \, wet} \] (where \( \gamma \) is the reaction order with respect to water) predicts apparent activation energies as high as 80 kcal/mol for the methane combustion using dry feed (e.g. for the low temperature data of Carstens et al. [7] where the uncorrected apparent activation energy is 42.8 kcal/mol, the corresponding corrected value would be 85 kcal/mol, which would dictate a physically unrealistic preexponential factor).

Our recent results [6] obtained with continuous flow of “dry” reaction mixture indicate higher apparent activation energy values for lower reaction temperatures and constant and lower values for higher reaction temperatures. We proposed that this effect is caused by a stronger inhibition effect of water at lower temperatures. These results are in agreement with those reported by Burch et al. [3] from pulsed experiments using “wet” reaction mixture. These authors
observed lower inhibition effect at higher temperatures and reported almost no inhibition effect of water molecules on the catalytic activity in pulsed reaction mode above 723K.

However, in previously reported [6] continuous flow experiments where water readsoption is important, feeding the reactor with “wet” reaction mixture led to important inhibition effects even at temperatures near the PdO thermal reduction. This stronger and temperature independent water inhibition effect was proposed to be strongly affected by the high time constant for the equilibration of the catalyst with respect to changes in the water concentration. The pulsed experiments presented here showed both time and temperature dependency of the water poisoning effect.

Firstly, the continuous desorption of water detected with the mass spectrometer as well as the delay in the water peak maxima clearly indicate that water molecules formed during the methane combustion reaction desorb slower than the other reaction products. It should also be noted that at 523K it takes 7 – 8 reaction mixture pulses until the water adsorption/desorption equilibrium at the catalyst surface is reached even with dry reaction mixture, suggesting the same high value of the time constant for the equilibration with respect to variations in the water concentration.

It is worthy to note that the delay in water peak maxima vs. temperature shows that water desorption from the catalyst is much slower at temperatures below 723K because water is desorbed after CO₂. This is consistent with our previous results [6] and with results reported by other authors [3]. It is also in agreement with the slow rate of water adsorption at the catalyst surface during the “wet” pulses of 1% oxygen in helium. These two experiments clearly indicate that the water that resulted from methane combustion lags the water introduced in the reactor with the gas feed. This is because during methane combustion reaction, water forms at the catalyst surface. Thus the surface is saturated with water and only desorption is important for the process kinetics at low temperatures. If water is present in the gas phase, desorption from the surface becomes even slower because the high partial pressure of water in the gas phase tends to accelerate adsorption.

Stronger evidence for the high value of the time constant for equilibration with respect to water concentration modifications comes from Fig. 2. While the TPR profiles obtained for continuous flow of “dry” and “wet” reaction mixtures are parallel, the profiles obtained using “dry” and “wet” reaction mixture pulses converge at about 773K, consistent with data reported by Burch [3]. The negligible inhibition effect observed for the first “wet” pulse in the TPR profile suggests a low water adsorption rate and, again, is consistent with the high value for the time constant of equilibration with respect to the time constant for water concentration modification. The proposed explanation is in agreement with the high methane conversion observed with the first “wet” feed pulse followed by the sharp decrease of activity observed for the subsequently injected “wet” pulses, as depicted in Fig. 3.

The long equilibration time could only be explained by means of activated adsorption for water molecules. This is consistent with the changes of the apparent activation energy of the methane combustion process observed at lower temperatures. However, the high values for the apparent activation energies reported for reaction conditions at which the water inhibition phenomenon is stronger suggest that water adsorption cannot be a pure physical process, but rather involves stronger, chemical like, binding energies between water molecules and PdO surface. Water inhibition at relatively high temperatures (723K for pulsed experiments and 900K for continuous flow of reaction mixture) suggests, thus that hydroxide formation as proposed by Burch [3] cannot be excluded.
Reaction of water molecules with metal oxide (001) surfaces (αAl₂O₃ and αFe₂O₃) was investigated by Chambers et al. [12]. These authors reported from Photo-Electron Spectroscopy investigation that for both oxides the hydroxyl groups more strongly bond on surface defects than on terraces, the chemical shift between these two species being as high as 0.3 eV for corundum and 0.7eV for hematite. Along these lines and assuming the methane dissociation on a Pd-O ions pair with the formation of a palladium-methyl pair and a hydroxyl group as proposed by Broclawik [13], the hydroxyl groups resulting from methane dissociation are likely to be stronger bound relative to hydroxyls resulting from water dissociation on the fully oxidized PdO surface. Following this rationale, measurements of water adsorption/desorption kinetics in the absence of methane could be misleading.

Conclusion

Equilibration of the interaction of water with palladium-based catalysts is slow with respect to the methane oxidation reaction time scale and the time scale for many TPR experiments, especially at low reaction temperatures. This is reflected in the inhibition of methane oxidation by water to higher temperatures in continuous TPR experiments than in pulsed reaction experiments and is important because it suggests that experiments with water in the feed cannot be used to predict the behavior of real systems and that results from temperature programmed reaction experiments can be biased. Therefore simply correcting the data for the water poisoning effect is not straightforward. A detailed microkinetic model of the methane oxidation mechanism must be employed to correctly predict transient and steady state performance of real systems.

Acknowledgements

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References
Table 1. Peak maxima (minutes) recorded for methane and reaction products for 10 successive reaction mixture pulses injected at equal time intervals at different temperatures.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Pulse #</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
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Figure captions

Fig. 1. Delay in water peak maxima determined with the mass spectrometer at different reaction temperatures with and without reaction.

Fig. 2. Temperature reaction profiles performed with “dry” (solid symbols) and “wet” (open symbols) under continuous flow of reaction mixture (circles) and reaction mixture pulses (squares in which the figures represent the pulses numbers).

Fig. 3. Methane conversions recorded at constant temperature (573K) for successive “dry” and “wet” reaction mixture pulses.
Fig. 1.
Fig. 2.

Methane conversion, %

Reaction temperature, K
Methane conversion, wt.%

- ■ Dry feed
- □ Wet feed

Pulse number

Fig. 3.
Short title: Combustion activity of partially reduced PdO

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Abstract

The activity of ceria-zirconia supported palladium catalysts for methane combustion has been found to be strongly dependent on the oxygen content of the PdO catalyst particles. Reaction mixture pulses of 1% methane, 4% oxygen and helium balance were injected over partially reduced catalysts obtained by chemical reduction with methane, and over completely reduced catalysts produced by thermal decomposition of the PdO phase. Catalyst activity was observed to initially increase with the degree of reduction, reaching a maximum and then decreasing continuously as the oxygen is depleted. The degree of chemical reduction is temperature dependent and at high temperatures, CO production is associated with extraction of subsurface oxygen.

Reoxidation of the completely reduced catalyst is slow and strongly inhibited, while the partially reduced catalysts reoxidize at higher rate. However, if a completely reduced layer forms on top of the oxide core, the reoxidation inhibition phenomenon is present and the reoxidation rate considerably decreases. At low temperature reaction conditions oxygen exchange from the bulk can be faster than reoxidation from the gas phase.

Keywords: methane combustion, palladium oxide, chemical reduction, thermal reduction.

Introduction

Palladium is a highly active oxidation catalyst for the complete combustion of a wide range of fuels including methane, other hydrocarbons, carbon monoxide and hydrogen. However, the catalyst activity for the combustion reaction changes significantly with reaction conditions and transient behavior including activity excursions and deactivation are not well understood.

In spite of the intensive research of the supported palladium catalysts, there is still a lack of agreement on many questions concerning the catalyst behavior during the reaction. Among other issues, activity as a function of oxidation state is not well understood, especially with respect to mixed states and transient operation. Oh et al. [1, 2] argue that the reduced Pd form is more active. Hicks et al. [3] observed that the activity of dispersed PdO is 10 to 100 times less than that of small palladium crystallites, and these authors [4] also observed that the oxide layer dispersed over the palladium crystallites is much more active than the palladium oxide dispersed over the alumina. Burch et al. [5 – 7], Farrauto et al. [8, 9], Primet et al. [10 – 12] and McCarty [13] consider the metal phase to be less active or completely inactive. A recent study by Lyubovsky and Pfefferle [14] shows that metallic palladium can be more active than PdO in the

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methane combustion reaction at higher temperatures and at stoichiometries near one and for fuel rich conditions. For a wide range of conditions, the catalyst activity has been observed to increase as the PdO is reduced or partially reduced. Positive activity excursions have been noted by many investigators in pulsed reduction by hydrogen or methane \([14, 15]\), and the activity hysteresis and transient excursions noted in laboratory and large scale experiments cannot be predicted a priori from any published micro kinetic mechanism.

In our earlier work \([16]\) we observed that there is lack of agreement between the palladium reoxidation temperatures observed in TGA and temperature programmed reaction (TPR) experiments and suggested that this difference may be due to the higher activity of the partially reduced / oxidized state of the catalyst. The results of the present work were obtained from pulse experiments with supported and unsupported palladium catalysts. The pulsed technique has the advantage that minimizes inhibition effects caused by readsoption of reaction products (i.e. water) and the oxidation state of the catalyst can be modified stepwise by injecting small amounts of reducing or oxidizing reactants. These results are used to study the correlation between the oxygen content of the catalyst and its methane combustion activity.

**Experimental**

The ceria-zirconia support was prepared using zirconyl nitrate hydrate and Ce(II1) nitrate precursors from Aldrich. Clear solutions of the precursors were mixed together and poured drop wise in ammonia under strong stirring. The precipitate was digested in ammonia for 120 hours, then filtered, washed with demineralized water several times and dried at 120°C for 12 hours in air. After drying, the solid was crushed and then calcined at 120°C for 6 hours in oxygen. According to our previous experience \([17]\) the resulting material is a crystalline solid solution containing 10% of ceria, and having a moderately high surface area.

Palladium nitrate was impregnated on the prepared support to give a catalyst with 3% of palladium. The impregnated support was further dried, and calcined under flowing oxygen at 500°C for 2 hours. This preparation produced a catalyst with approximately 10 nm PdO particles. In reaction strategy used catalysts are reduced at 900°C and cooled under continuous reaction mixture at 5°C/min to 360°C. Repetition of this process produces PdO particle sizes from 15-25nm but these particles from UV-vis analysis and previous HRTEM studies are made up of smaller crystalline domains on the order of 5nm (see for example \([18]\)). This form of catalyst is stable for long term catalyst operation and many oxidation/reduction cyclings as performed in these studies. This is confirmed by earlier work using HRTEM \([19]\) and TPR experiments \([16]\) and in this study by a return to the initially observed low temperature activity. Although it is not possible to directly monitor surface state under high pressure conditions, we did carry similar pulsed and continuous flow experiments in a reaction cell placed in the diffuse reflectance accessory of an HP8452A UV-vis spectrometer. This experimental setup allows measuring the band gap energy of the catalyst in situ, thus the oxidation state of the bulk catalyst.

In past studies \([16]\) we showed that a high oxygen mobility support can accelerate the reoxidation of PdO after reduction. For comparison purposes, pure PdO (99.999%) from Aldrich was also used.

Approximately 50 mg of fresh supported catalyst was loaded into an alumina tubular reactor with 4mm internal diameter. The reactor was placed in an electric heater equipped with automatic temperature controller. The experimental setup allows the reactor to be operated both in continuous reaction mixture flow mode, and in pulse mode. The pulse mode consists of
reaction mixture pulses injected in the helium carrier stream that flows continuously through the catalytic bed. The switch from one mode to another can be accomplished in a minutes time scale.

Before each experiment the supported catalyst was cycled under continuous flow of reaction mixture (CH$_4$:O$_2$:He = 1:4:95 from Airgas) between room temperature and 900°C at a 5°C/min heating/cooling rate. As discussed elsewhere [16], this treatment enables the catalyst to preserve a constant activity vs. time on stream for more than 24 hours.

The reaction products were analyzed in a gas chromatograph equipped with methanizer and FID. This analytic setup allows determining the carbon oxides (CO and CO$_2$) and the unreacted methane concentrations in the reactor effluent.

For the isotopically labeled experiments (1% CH$_4$, 4% $^{18}$O$_2$ in He), reactor effluent was sampled through a heated capillary pipe to a HP5971A mass selective detector, which allowed measuring the distribution of the reaction products isotopomers.

**Results**

Prior to the pulsed reaction tests, the catalyst was heated to 900°C and then cooled at 5°C/min under continuous flow of reaction mixture to 360°C. At these reaction conditions the steady state methane conversion, expressed as concentration of CO$_2$ produced versus the initial concentration of methane, was determined as depicted in the region (a) of Fig. 1. After a 30 minute stabilization period the reaction system was switched to pulse mode – region (b) in Fig. 1 – and consecutive reaction mixture pulses were injected at 5 minutes equal time intervals, if not otherwise specified. After several pulses, the catalytic activity stabilized at a considerably higher level than for the continuous mode, most likely because of the lower inhibitory effect of water under pulsed reaction conditions [6, 7, 16]. After the methane conversion stabilized the pulse series was interrupted for 14 hours (point A in Fig. 1). During this time the helium carrier flowed continuously over the catalyst. The pulse series break produced only a small and temporary increase of the methane conversion, after which the catalytic activity returned to the value before the break, indicating the oxidation state of the catalyst does not change significantly under helium flow (<1 ppm oxygen levels) at temperatures below 400°C. This was also confirmed by a similar experiment performed in the reaction cell placed in the UV-vis spectrometer.

When the reaction mixture pulses were replaced with pure methane pulses – region (c) in Fig. 1 – the first pulse gave CO$_2$ amounts near the detection limit and the following two pulses gave undetectable amounts of carbon oxides. The UV-vis spectra indicates the catalyst is partially reduced. The methane pulses were again replaced with pulses of reaction mixture and the methane conversion changed as shown in the region (d) of Fig. 1. The activity rapidly increased to values recorded before catalysts reduction, reached a maximum and then decreased to undetectable values after 16 reaction mixture pulses. The pulse series was again interrupted for 15 minutes (points B in Fig. 1) and then resumed. Again high initial activity was observed, which rapidly decreased with the number of pulses. This behavior was completely reproducible, so that after a longer break (point C in Fig. 1 corresponds to 90 minutes break) the catalyst mirrored the behavior observed immediately after methane reduction. This is likely a result of reduction of the surface layers during reaction (uptake of oxygen from the gas phase is slow) and replenishment of the surface with bulk oxygen in the pause period as also observed in our earlier work with isotopically labeled oxygen [20]. This was confirmed in a separate run with isotopically labeled oxygen described below. When the reaction system was switched back to continuous flow at the end of the experiment – region (e) in Fig. 1 – the catalyst recovered its initial activity on a time scale of tens of minutes (see region (a) of Fig. 1), but the catalyst was
still partially reduced as indicated by the UV-Vis spectrum indicating that reoxidation is slow under these conditions as noted in our work and that of others [19, 21].

For the next experiment, the catalyst was again cycled to 900°C and was cooled down at 5°C/min in flowing reaction mixture to 360°C. After the catalyst activity at this temperature was constant under continuous flow conditions (region (a) in Fig. 2), the system was switched to pulse mode and a stable conversion was observed for 10 consecutive pulses, as plotted in region (b) in Fig. 2. This time, instead of pure methane pulses for the catalyst reduction, pulses of a mixture of 1% methane in helium were injected and the methane conversion changed with the number of pulses as depicted in the region (c) of Fig. 2. The methane conversion increased, reached a maximum, and then started to decrease. In region (d) of Fig. 2 the reaction system was switched to continuous flow of 1% methane in helium until no CO or CO₂ were detected in the reactor effluent (about 30 min). Then the reaction system was switched back to pulse mode – region (e) in Fig. 2 – and reaction mixture pulses were injected at the same time interval. Again, the catalyst mirrored the behavior observed after reduction with pure methane – see region (d) in Fig. 1. However, after reaching the minimum, the catalyst activity started to recover at a stable low rate.

The same experiment performed with unsupported PdO at 390°C gave similar results (see open symbols in Fig. 2(c)), indicating the increase in catalyst activity observed with slightly reduced PdO catalysts is not caused by the support. However, a reducible support is likely to influence this behavior by supplying oxygen to the partially reduced PdO phase.

After the test described in Fig. 2, the supported catalyst was again cycled to 900°C in the reaction mixtures and cooled to 390°C. Then a similar test was performed at this temperature showing the same qualitative behavior, as can be observed in Fig. 3. After activity stabilization under a continuous flow mode – region (a) in Fig. 3 – the system was switched to pulse mode and reaction mixture pulses were injected – region (b) in Fig. 3 – until a fairly constant conversion was observed. Then three pure methane pulses were injected for catalyst reduction, as depicted in region (c) of Fig. 3. After reduction, reaction mixture pulses were injected at 5 minutes time intervals and the conversion changed as plotted in region (d) of Fig. 3. An initially high activity is observed, followed by a sharp decrease, and recovery to approximately the oxidized state. TR in Fig. 3 indicates where the catalyst was thermally reduced (heating to 900°C and holding at this temperature for 30 minutes under flowing helium). This procedure was shown in previous work [19] to produce a completely reduced catalyst. After the thermal reduction, the catalyst was cooled down to 390°C in helium flow and the reaction mixture pulse series was resumed at this temperature – see region (e) in Fig. 3. The activity increased gradually to reach a plateau after about 20 pulses. It should be noted that the plateau activity is higher than that observed before reduction at the same reaction conditions in the region (b) of Fig. 3.

Although the general trend is similar to the one in Fig. 1, there are a few differences in the behavior of the catalysts. First, for the same amount of catalyst, the amount of methane consumed during reduction at 390°C, as measured by the amount of CO₂ produced – region (c) in Fig. 3 – was higher than that consumed at 360°C showing a higher degree of reduction. Then, the activity peak observed after catalyst reduction is considerably higher than the value observed with reaction mixture pulses on the completely oxidized catalyst – region (b) of Fig. 3.

After a new cycling to 900°C in reaction mixture, the catalyst was cooled in flowing reaction mixture at 490°C. Again after constant conversion under continuous flow mode stabilized (region (a) in Fig. 4), the system was switched to pulse mode and reaction mixture pulses were injected until constant conversion was observed – see region (b) in Fig. 4. The
catalyst was then reduced with pure methane pulses. In region (c) the CO and CO$_2$ concentrations during the reduction by 6 successive methane pulses are depicted. After reduction, the series of reaction mixture pulses was resumed and the carbon oxides concentrations observed for successive pulses are depicted in the region (d) of Fig. 4.

There are two important new features compared with the results obtained for similar experiments at lower temperatures (see Fig. 1 and 3). First, CO production was observed both during methane reduction, and when the reaction mixture pulse series was resumed with the chemically reduced catalyst. Second, after reaching the minimum activity with reaction mixture pulses, the reduced catalyst recovered only a few percent of its initial activity and stabilized at a much lower conversion than that observed with the completely oxidized catalyst.

Another notable observation is the difference between the catalyst activity under the continuous flow regime and pulse regime. At 360°C the activity of the catalyst under the pulse regime is about four times higher than under continuous flow of reaction mixture. When the reaction system was switched between the two regimes at 490°C, an increase of only 15% of activity was observed. This behavior is consistent with other work showing a lesser inhibition effect of water at higher temperatures, although equilibration time, the support and other factors likely play a role [22].

In order to determine the reoxidation behavior under pulsed reactant flow at the temperatures of these experiments, the catalyst was thermally reduced at 900°C cooled in He to 600°C and subjected to reactant pulses as described above. The methane conversion activity of the catalyst on a stepwise cooling ramp from 600°C is depicted in Fig. 5. Since the catalyst activity decreased with the reaction temperature between 600°C and 550°C, we associate this activity with the metallic state of the catalyst. The temperature was decreased in a stepwise fashion until an increase in conversion was observed. At that moment the temperature was held constant and consecutive reaction mixture pulses were injected until constant conversion was observed. The catalyst activity has been shown in many previous studies [8, 9, 13, 16, 18] to increase with the progress of catalyst reoxidation. The thermally reduced catalyst did not reoxidize on the time scale of this experiment until the temperature was decreased to 460°C, although under continuous flow of reaction mixture (not shown) the onset of the activity recovery was observed at 690°C. This suggests that in the final part of region (d) in Fig. 4 the low activity of the catalyst was due to incomplete reoxidation to crystalline PdO.

A last run was carried out over a 3% Pd/zirconia supported catalyst using $^{18}$O$_2$ instead of $^{16}$O$_2$ in the reaction mixture. The purpose was to assess the proposal that oxygen from the bulk was important in oxidizing the methane for the data in Fig. 1 region (d) and Fig. 2, region (c) and that surface oxidation from the gas phase can be slower than oxygen exchange from subsurface layers under these reaction conditions. After being cycled to 900°C in the reaction mixtures and cooled to 365°C, the catalyst was exposed to reaction mixture pulses containing 1%CH$_4$ and 4% $^{18}$O$_2$. After reactivity had stabilized (Fig. 6, region (a)), the catalyst was partially reduced with diluted methane pulses – region (b). During reduction, reactivity increases to a maximum and then falls, consistent with the behavior observed for the earlier runs. Reaction mixture pulses were then resumed after a 9 minute pause (region (c)). Initially all of the oxygen in the CO$_2$ and water comes from the $^{16}$O originally in the catalyst rather than from the $^{18}$O from the gas phase. This is consistent with our earlier study showing that only one type of oxygen (lattice) is used for methane oxidation [20]. Even at the last reaction pulse in region (c), only 11% of the CO$_2$ contains $^{18}$O. The water contains considerably less $^{18}$O than the CO$_2$ (note the x10 scale change for water). This is again consistent with our earlier work [20] showing that hydrogen samples the
bulk and thus water reflects the bulk isotopic distribution of the catalyst. Reaction mixture was then paused for 30 minutes after which the reaction mixture pulses were resumed. At this point reactivity again increased dramatically and the fraction of $^{16}O_2$ in the products increases likely because of oxygen exchange from the bulk to the surface. The catalyst is being reoxidized slowly from the gas phase as indicated by the increase of $^{18}O$ in the products. The surface, however, is likely being depleted of oxygen during reaction as replacement from the gas phase competes with reoxidation of the bulk, and consumption of lattice oxygen by reaction. This catalyst was previously tested for oxygen exchange with the support which was found to become important under these pulsed reaction conditions at temperatures somewhat above that used here. The temperature where oxygen exchange with the support becomes fast is lower for continuous flow conditions. If oxygen exchange with the support were important here or for the catalyst used in Fig. 1, however, the reactivity would not fall with pulse number.

Because a potential source of the activity excursion after catalyst reduction could be due to carbon deposited on the catalyst surface, an experiment was also performed to check for the presence of carbonaceous deposits after reduction. Pure oxygen pulses injected over the pure methane reduced catalysts generated very small amounts of carbon dioxide. However, the resulting CO$_2$ was undetectable using the detector sensitivity at which the pulse tests were performed. As a secondary check method, the total peak areas resulting for the chromatograms obtained during the activity excursion were fairly constant. Consequently, the CO$_2$ concentrations recorded for reaction mixture pulses over the reduced catalyst resulted from methane combustion and not from surface carbon deposits oxidation. Carbon on the surface could, however have moderated activity excursions observed after reduction with pure methane.

The results of the UV-vis experiments carried out from 350 to 550°C can be summarized as follows:

- the catalyst is not reduced in helium flow at the temperatures and time scales of the pulsed experiments where the activity excursion were observed;
- the catalyst was not observed to be reduced during reaction mixture pulses or during continuous flow of reaction mixture;
- once the catalyst was slightly reduced by diluted methane pulses at 365°C, as much as 34 subsequent reaction mixture pulses do not completely reoxidize catalyst;

Discussion

Methane combustion activity excursions were previously reported following catalyst reduction with hydrogen or methane [14, 15]. Bell and co-workers [15] observed that hydrogen pulses injected in the reaction mixture stream flowing continuously over the zirconia supported PdO catalyst at temperatures in the 125 - 180°C range produced a noticeable increase of the CO$_2$ production rate. However, after a certain number of hydrogen pulses, the catalyst activity dropped to zero, even at 180°C where the activity of the catalyst before hydrogen pulses was higher than zero, suggesting that a large degree of reduction eventually produces catalyst deactivation. The authors claimed that CH$_4$ is not activated on PdO at low temperatures and ascribed the activity excursions to the formation of small amounts of Pd on the surface of PdO. They also claimed that the presence of metallic palladium in close contact with PdO greatly enhanced the rate of reduction of PdO by methane and argued that it occurs via a nucleation mechanism that requires the presence of metallic palladium [23]. However, the authors did not provide any experimental evidence of the presence of metallic palladium on the catalyst under
the experimental conditions used. In previous work we and other authors have shown that a nucleation mechanism is likely [18, 19, 24].

A nucleation mechanism followed by oxygen transport limitations form the bulk would explain the increase followed by decrease in reactivity during reduction with diluted methane. First the surface layers are completely reduced then the rate of reduction is limited by transport of oxygen from bulk to the surface. Reduction with hydrogen results in constant conversion per pulse [20]. With diluted methane pulses, however, conversion during reduction of PdO varies dramatically pulse to pulse (see Fig. 2). At low temperatures and mild reduction conditions the surface is reduced gradually. At these conditions methane conversion can increase on subsequent pulses before decreasing when the reduction process becomes limited by transport of oxygen to the surface. At high temperatures where the surface layers are completely reduced on the first pulse, conversion continually decreases because reaction is limited by transport of oxygen to the surface or by reoxidation from the gas phase. This is clearly shown in the data of Fig. 6.

In related work we showed that a single form of oxygen is likely responsible for reactivity at the conditions where the PdO phase is stable [20]. These results do not, however, rule out the possible role of mixed phases under some reaction conditions. Studies of the oxidation of metallic Pd indicate that the reaction can be slow [2, 5]. In addition, at low temperature reaction conditions reoxidation from the bulk can be faster than from the gas phase. This creates a steady state of vacancy states. The above arguments suggest that Pd and PdO can coexist for extended periods at certain temperatures and oxygen pressures, which is not thermodynamically possible if equilibration with the gas phase is rapid. We and other researchers have shown that during methane oxidation reaction, surface reoxidation/oxygen exchange with the gas phase is slow. In earlier work using high resolution transmission electron microscopy (HRTEM) we observed that in transient conditions the surface can likely consist of a patchy array of phases [19]. Previous TPD and STM results of Zheng and Altman [24] show a sequence of four phases during Pd oxidation, confirming at least one stable intermediate state. Along these lines, at any point in time the condensed phases can be described by oxygen-palladium mole fractions. Since both the miscibility of oxygen in Pd and the oxygen deficiency of PdO are limited, separation of the Pd and PdO phases will occur. The mixed Pd-O surface would exist at the interface between the two bulk phases. The phase with the lowest surface tension would tend to completely encapsulate the higher surface tension phase. Since oxides typically have lower surface tensions than metals, reduced Pd clusters formed during the reaction of methane with lattice oxygen at the PdO surface are likely to be encapsulated by the bulk oxide phase. The encapsulation mechanism likely consists of bulk oxygen diffusion towards the surface, thus in equilibration of the concentration of the vacancies between surface and bulk. This is consistent with our experimental observation that, at certain operating conditions, oxygen equilibration between the condensed phases can be fast compared to equilibration with the gas phase. Hence, Pd and PdO may coexist for an extended duration, even at high temperatures. These factors may affect reactivity when the catalyst is reduced and then exposed to reaction mixture as in the experiments described here.

An important question that needs to be addressed is whether the chemical reduction with methane generates the same state of the catalyst as the thermal decomposition of PdO. It should be mentioned that the amount of methane consumed in the experiments where pure methane was used to reduce the catalysts is below the stoichiometric amount necessary for the complete reduction of the PdO catalyst, assuming the whole amount was consumed by the palladium oxide. Moreover, the amounts of methane consumed at different temperatures were different for
the same amount of catalyst: at 360°C only traces of CO₂ were detected, while at 390°C the CO₂ concentration in the reactor effluent after the first methane pulse was considerably higher, and at 490°C the oxygen balance suggests the bulk catalyst is highly reduced. At 490°C, although the catalyst may be fully reduced, oxygen from the support could also be removed in the presence of Pd (pure zirconia does not reduce); however, we have shown in related research [20] that exchange of oxygen between zirconia and Pd under these pulsed reaction conditions becomes fast at 425°C. Consequently, the degree of the catalyst reduction with methane increases with the temperature. Based on the results presented here, we propose that, in contrast with the thermal reduction, the chemical reduction proceeds from the surface towards the particle bulk, thus forming a reduced layer on top of an oxide core.

It should also be noted that, in a separate experiment, continuous flow of 1% of methane in helium for three hours at 360°C did not completely reduce the palladium oxide phase, but produces partially reduced PdO particles as observed by UV-vis spectroscopy. After this treatment the catalyst showed the same activity excursion (see Fig. 2). This suggests the energetic barrier for reduction increases with the degree of reduction, most likely because of the low diffusion rate of the bulk oxygen at low temperatures. Meanwhile, the reduced surface layer could also be less permeable for oxygen than palladium oxide, thus acting as a diffusional barrier.

Formation of CO during reduction at high temperature suggests that the oxygen species extracted by the methane molecules are available at a lower rate, likely due to diffusion limitations from the bulk. Comparing the temperature reduction profiles obtained using methane as reducing agent for catalysts pretreated at different conditions, Muller [25] proposed the existence of several kinds of PdO having different reactivities for the reduction with methane. In agreement with the "reduced layer on top of an oxide core" proposed model, extraction of the oxygen from the subsurface layers has a higher energy barrier than that for the surface oxygen, and has a lower rate than surface oxygen depletion. Under these circumstances, the CO formed as intermediary oxidation product is desorbed from the surface before being completely oxidized. However, since at the higher temperatures required for the subsurface oxygen extraction the oxygen mobility is higher, a contribution of the oxygen from the support cannot be completely ruled out.

The catalysts that were partially reduced using methane pulses behaved completely differently in the combustion reaction when compared with the catalysts that were fully reduced by thermal decomposition of the PdO phase. The initial combustion activity of the chemically reduced catalyst is much higher than that of the thermally reduced one, but this high activity rapidly decreases to a minimum and then increases again – see Figs. 2, 3 and 4. In contrast, the thermally reduced catalyst had a low initial combustion activity, which gradually increased to reach a plateau value higher than that observed at the same reaction conditions before reduction (see Fig. 3), consistent with the activation noted in cycled TPR experiments. The catalyst reduced with methane at 490°C (Fig. 4) showed formation of carbon monoxide when exposed to reaction mixture pulses after the reduction step, despite the presence of excess oxygen in the pulses. This behavior suggests that only lattice oxygen is used for methane oxidation, and the uptake of gas phase oxygen is slow, consistent with data in Fig. 6. Therefore, the amount of oxygen in the PdO layers near the surface accessible for the methane molecules at this temperature is not enough to completely oxidize the methane fragments resulted from dissociation of the methane molecules. This explanation is consistent with previous results [20] showing diffusion of oxygen from the bulk can be the rate limiting step for methane combustion.
Following thermal decomposition, completely reduced palladium particles are obtained. Their initial catalytic activity for the methane combustion reaction is low and increases as the catalyst is oxidized with oxygen from the reaction mixture pulses – see Fig. 3 – in agreement with previous temperature programmed reaction results [16]. The chemical reduction process generates a different catalytic surface that is more reactive for methane combustion, but which deactivates with the number of reaction mixture pulses injected. The chemically reduced catalyst also reoxidizes more rapidly than the thermally reduced one. This is consistent with observations that catalysts that are only partially reduced reoxidize quickly while those fully reduced show an inhibition to reoxidation when cooled. It is unclear yet whether the surface reduced layer produced by chemical reduction consists of metallic palladium or an intermediate PdO, phase with x<1. However, the initial activity of the chemically reduced catalyst increases with the degree of reduction until reaches a maximum, after which decreases as the oxygen content of the catalyst decreases - see region (c) of Fig. 2.

On the other hand, the activity of the completely oxidized palladium catalyst stabilized at lower value than the steady state activity of the thermally reduced and reoxidized particles – see Fig. 3. An explanation for this activation associated with the reduction/reoxidation process consists in the higher temperature for catalyst reoxidation during cycling in reaction mixture than that of the current experiment. During the cooling down ramp, at the oxygen partial pressure corresponding to continuous flow of reaction mixture at atmospheric pressure, the onset of the catalyst reoxidation was observed at about 690°C. Once the oxide particles are formed at higher temperature, their mobility is high and possibly sinter to give larger PdO particles and lower catalytic surface area. Reoxidation at lower temperature has been shown to produce small PdO, cauliflower – like domains [18]. These form during surface rearrangements caused by density differences between the metallic and the oxide phases. These structures are less likely to sinter because of the lower oxidation temperature and, therefore, give higher surface density of the catalytic sites.

With respect to the kinetics of the two reduction processes, Voogt [26] proposed a linear decrease in time of the PdO core radius until the last layer of oxide at the surface. They suggested that formation and desorption of molecular oxygen at the catalyst surface is the rate limiting step of the PdO thermal reduction. However, because of the presence of methane in the reaction environment at the actual operation conditions of the catalyst, the extraction of the surface oxygen is accelerated by reaction with methane, as demonstrated by several mechanistic studies [21, 25]. For this reason, the bulk oxygen diffusion is most likely to become the rate limiting step for the PdO phase decomposition.

In the case of chemical reduction with methane, after the initial reduction of surface layers, the oxygen diffusion from the bulk likely controls the reduction process kinetics. Indeed, as observed in the region (c) of Fig. 2, once the surface oxygen is depleted with small, successive methane pulses, the combustion activity initially increases and then decreases, most likely because of the lack of the oxygen at the surface. However, the catalyst behavior after the breaks in the pulse series (points B and C in region (d) of Fig. 1) are likely due to the refilling of the reduced surface states with oxygen from the particle bulk in the absence of oxygen in the gas phase as shown from the experiment illustrated in Fig. 6. Since the amount of oxygen accumulated at the catalyst surface after a 15 minute break (point B in Fig. 1) is depleted in 5 pulses of reaction mixture, while that accumulated after 90 minutes break (point C in Fig. 1) needed 11 reaction mixture pulses to be exhausted, the process of oxygen refilling of the reduced surface is slow, and the amount of bulk oxygen that reaches the reduced surface of the palladium
phase at low temperatures needs a long time to equilibrate. Oxygen can also come from the catalyst support through a spill over mechanism from ceria – zirconia support toward the palladium phase of the catalyst. The rate of exchange of oxygen with the bulk, the gas phase and the support is highly temperature dependent. In another study we found that at temperatures below about 350°C bulk Pd⁴⁰O and Pd⁴⁰O supported on zirconia showed the same isotopic oxygen exchange rate when exposed to a reaction methane /¹⁸O₂. Breaks in the pulses on the minute time scale (He flowing over the catalyst) replenished the ¹⁶O on the surface. At higher temperatures, however, oxygen exchange with the zirconia support became important dominating at temperatures near 425°C.

From the reoxidation point of view, the degree of reduction is observed to be critical for the reoxidation rate, but the temperature is also important. As seen in Fig. 5, the completely reduced catalyst did not reoxidize with reaction mixture pulses at temperatures above 460°C. The reoxidation temperature is different from the one previously reported from temperature programmed reaction experiments [16], which was found to be as high as 690°C. The difference is due to the higher average oxygen partial pressure at the TPR reaction conditions. This result also shows the often observed inhibition of reoxidation phenomenon. As oxygen partial pressure is lowered the threshold temperature where significant oxidation takes place is also lowered. The initial stage of reoxidation has been proposed to consist of the formation of a strongly bound surface oxide state whose concentration does not change in time at constant temperature, as reported by Datye [18]. This structure is likely to block the access of oxygen towards the particle bulk and probably has low activity for methane combustion. McCarty [13] proposed that the energy of formation of chemisorbed oxygen might be so much greater than that of the bulk oxide that a full monolayer of relatively passive chemisorbed oxygen forms over the metallic particle inhibiting both reaction and oxygen absorption. As temperature is decreased the reoxidation rate first increases and then decreases consistent with the above mechanism. This is also supported by recent studies of Pd (110) oxidation by Zheng and Altman [24]. They observed in their STM study that the palladium oxidation using NO₂ underwent three steps: (i) rapid adsorption; (ii) oxygen penetration into the surface accompanied by island growth leading to the formation of two phases that are intermediate between Pd and PdO; (iii) formation of bulk PdO. Using TPD, these authors found that the heat of adsorption (first step of the proposed mechanism) assuming a second order desorption of oxygen was -50.2 kcal/mol, significantly higher than the 25.65 kcal/mol heat of formation of PdO [27], in agreement with previous results of McCarty.

The reoxidation rate of the chemically reduced catalyst was observed to be temperature dependent increasing and then decreasing as temperature increases, consistent with the many temperature programmed reaction studies showing “negative activation” [8, 9, 13,16 and references therein]. At 360°C the activity recovered about 50% of the initial activity before reduction when exposed to reaction mixture pulses (compare Fig.2 regions b and e) consistent with UV-vis showing the catalyst was not fully reoxidized. As shown in Fig. 1, however reactivity was restored after exposure to a continuous flow of reaction mixture for several minutes. During the run at 390°C, however, activity recovered over 90% of the pre-reduction value in a fewer number of pulses even though the degree of reduction was greater (regions (b) and (d) in Fig. 3). On the other hand, the catalyst chemically reduced at 490°C did not recover the activity level prior to reduction, suggesting the same inhibitory effect as observed for thermally reduced catalyst on cooling from high temperature. This is consistent with the data shown in Fig. 5 where the thermally reduced catalyst could not be oxidized by reaction mixture pulses until the temperature was lowered to 450°C. At 490°C CO formation was observed both
during catalyst reduction and at the beginning of the reaction mixture pulses following the reduction. Since CO production has been associated with extraction of the oxygen from the subsurface layers, a reduced skin behaves as a metallic layer on top of a PdO core, likely showing the same strong oxygen chemisorption as described by McCarty. Under these circumstances as the surface is oxidized from the gas phase a sandwich structure of a metallic layer between two oxide layers would form. The slightly higher activity of this structure compared with the metallic particle is probably due to the oxygen diffusion from the PdO core toward the metallic layer that enables some of the strongly bound surface oxygen molecules to interact with methane molecules from the gas phase. Also, because the structure of the electronic bands of the thin reduced layer at the catalyst surface is likely to differ from the one of pure metallic particles, the binding energy of the chemisorbed oxygen is likely to be weaker.

Previous studies of both alumina and zirconia supported palladium catalysts under continuous flow reaction conditions have shown higher positive activity excursions induced by chemical reduction of the surface [14, 15, 23]. These showed lifetimes for the activated state from minutes to hours. These continuous flow studies, however, convolute the impact of the reduction on water poisoning with other mechanisms that could increase or decrease reactivity. In addition most were carried out at higher temperatures where reoxidation of the reduced layer can be very slow.

Conclusions

The thermal reduction of PdO in this study produces completely reduced, metallic particles, while the chemical reduction with methane pulses allows partial reduction of the catalyst. For equivalent amounts of methane injected over the catalytic bed, the degree of reduction depends on the temperature. High reduction temperatures allow the subsurface oxygen to be extracted.

The activity of the chemically reduced supported palladium catalyst for methane combustion has been found to experience important changes with the modification of the oxygen content of the catalyst. Slightly reduced samples were observed to be more active for methane combustion than either completely oxidized or metallic particles. This is consistent with studies showing fuel rich oxidation over PdO (under conditions where PdO is the stable phase) to have a much higher specific activity than under excess oxygen conditions. Isotopic labeling experiment showed uptake from gas phase is slow in the presence of methane oxidation and also confirms single type lattice oxygen used to oxidize methane.

The activity of the catalyst under the pulsed mode was significantly higher than under continuous flow mode as expected from our previous understanding of water poisoning. A comparison of Fig. 1, 3 and 4 shows that this difference becomes smaller as temperature is increased, consistent with the degree of water poisoning decreasing with temperature.

The completely reduced ceria-zirconia supported palladium catalyst is more difficult to reoxidize than the partially reduced one. Therefore, if the thermal decomposition of an industrial catalyst would be stopped before completion, the activity hysteresis could be prevented because of the higher rate of reoxidation of the partially reduced catalyst. The presence of CO in the combustion products is likely associated with the initiation of bulk PdO reduction.

Reoxidation of catalysts that had been completely reduced and then exposed to reaction mixture pulses gave evidence of the inhibition of reoxidation described by McCarty [13]. Because this effect has been shown to be support dependent when palladium particle size is held
Appendix III

constant [16] the role of the support may provide an important clue to why reoxidation is inhibited.

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References
Appendix III

Figure captions

1. Methane combustion activity of a ceria-zirconia supported palladium catalyst with reaction mixture pulses; (a) continuous reaction mixture flow; (b) reaction mixture pulses; (c) pure methane pulses; (d) reaction mixture pulses; (e) continuous flow of reaction mixture. Points A, B and C stand for brakes in the pulse series of 14 hours (A), 15 minutes (B) and 90 minutes (C), respectively.

2. Methane combustion activity of the stepwise reduced ceria-zirconia supported catalyst; (a) continuous flow of reaction mixture; (b) reaction mixture pulses; (c) pulses of 1% of methane in helium, open symbols, reduction with 1% methane in helium for a bulk PdO catalyst; (d) continuous flow of 1% of methane in helium; (e) reaction mixture pulses.

3. Methane combustion activity of chemically and thermally reduced catalyst; (a) continuous flow of reaction mixture; (b) reaction mixture pulses; (c) pure methane pulses; (d) and (e) reaction mixture pulses. TR indicates the catalyst was thermally reduced.

4. CO and CO2 concentration in the reactor effluent after reaction mixture pulses over the thermally reduced catalyst; (a) continuous flow of reaction mixture; (b) reaction mixture pulses; (c) pure methane pulses; (d) reaction mixture pulses.

5. Methane conversion observed after injecting reaction mixture pulses at different temperatures over the thermally reduced catalyst.

6. Methane conversion and distribution of the \(^{18}\)O isotope among the reaction products following labeled reaction mixture pulses over a partially reduced Pd\(^{16}\)O catalyst; (a) unlabeled reaction mixture pulses; (b) pulses of 1% methane in He; (c) and (d) labeled reaction mixture pulses. The first series of labeled reaction mixture pulses was injected following a 9 minutes pause after reduction, and between (c) and (d) the catalyst was held under He flow for 30 minutes.
Fig. 2

Methane conversion, wt.%

Pulse number

- Supported PdO (360°C)
- Unsupported PdO (390°C)
Fig. 4
Fig. 5
Fig. 6.