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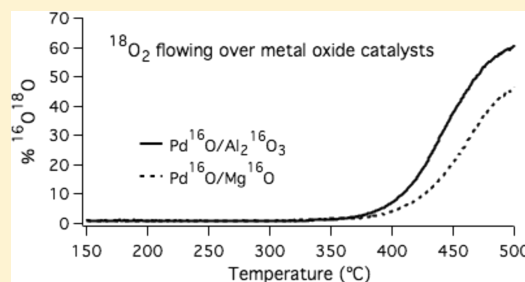
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# Combustion of Methane over Palladium-Based Catalysts: Support Interactions

William R. Schwartz\* and Lisa D. Pfefferle

Department of Chemical Engineering, Yale University, New Haven, Connecticut 06520, United States

**ABSTRACT:** Palladium-based catalysts are attractive for methane combustion at low temperatures, although deactivation is an issue, making it important to understand the mechanism for the catalytic combustion reaction. Support effects on the catalytic combustion reaction were investigated at temperatures below 450 °C using continuous flow of CH<sub>4</sub> plus <sup>16</sup>O<sub>2</sub> or <sup>18</sup>O<sub>2</sub> over various combinations of isotopically labeled PdO/metal oxide catalysts. Our experimental results are consistent with a PdO/Pd redox combustion mechanism. However, the oxide supports are also shown to provide oxygen for the catalytic combustion reaction. Pd/PdO serves as a porthole for gas phase oxygen to dissociate, migrate to the oxide support, and exchange with oxygen from the oxide support. The migration and exchange process allows oxygen that was originally bonded to the support to participate in the catalytic combustion reaction. Water, a reaction product, inhibits the exchange of oxygen between the support and PdO. The rate of oxygen exchange is temperature and support dependent. Mechanisms for the low temperature combustion of methane over PdO-based catalysts need to include steps for oxygen and hydroxyl exchange between the Pd phase and the support.



## INTRODUCTION

Methane oxidation over palladium-based catalysts has been extensively studied and reviewed, due to its attractive potential for catalytic combustion with low polluting emissions.<sup>1–4</sup> The catalytic reaction occurs with virtually no CO, unburned hydrocarbon or soot formation, and at reaction temperatures allowing virtually no thermal production of NO<sub>x</sub>. Additional benefits include lower CO<sub>2</sub> production per unit of energy for methane compared to other hydrocarbon-based fuels, and a plentiful methane supply when fossil fuels become scarce. Despite extensive study, issues still remain concerning the mechanism for the underlying catalytic combustion reaction. In this study, we focus on the role of the support in the catalytic combustion reaction.

Isotopic oxygen studies by Muller et al. at temperatures from 300 to 500 °C suggested that the combustion reaction on ZrO<sub>2</sub> supported PdO catalysts proceeds partly via a redox Mars and van Krevelen mechanism<sup>5</sup> but that the overall conversion is determined by the interplay between the surface reaction of adsorbed reactants and the redox mechanism.<sup>6,7</sup> In Mars and van Krevelen redox reactions, oxygen from the metal oxide catalyst is utilized in reaction, and gas phase oxygen then reoxidizes the reduced metal oxide. Muller et al.<sup>7,8</sup> also found that overall catalytic activity is influenced by contact of the palladium phase with the support, which affects particle size, surface area, and the quantity of active catalytic sites.

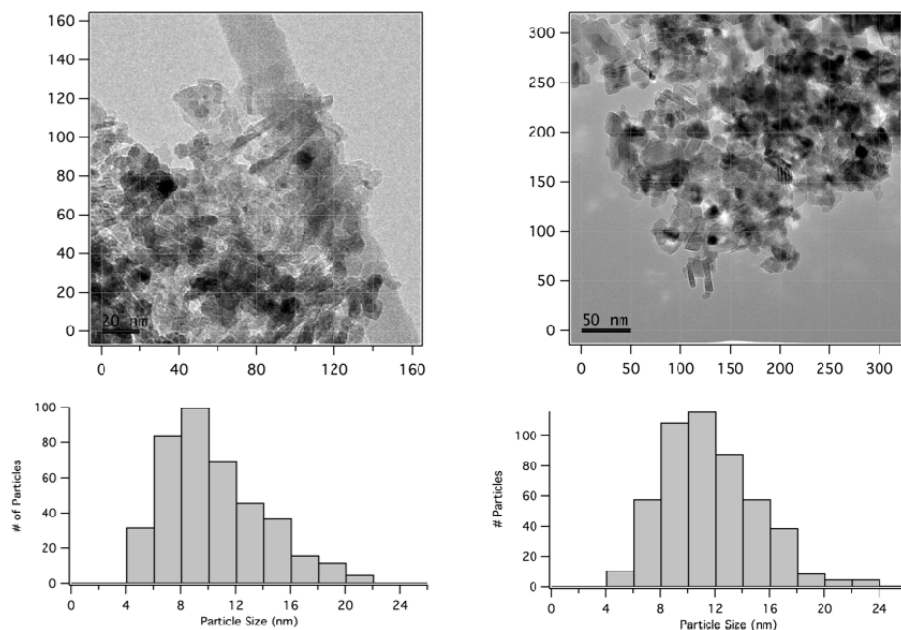
A number of other studies have supported the occurrence of a Mars and van Krevelen redox-type mechanism during methane combustion over palladium-based catalysts.<sup>9–12</sup> Though the redox mechanism is likely an important component of the overall catalytic oxidation reaction, a more

complete catalytic oxidation model must include the role of the support. Early studies on the hysteresis effect during methane combustion over palladium-based catalysts at high temperature suggested involvement of the support.<sup>13,14</sup> Farrauto et al.<sup>14</sup> observed that the decomposition and reformation of PdO species (PdO → Pd → PdO), and thus its catalytic activity for methane oxidation is strongly dependent on the nature of the support. Datye et al.<sup>15</sup> proposed that the oxidation of Pd is influenced by interfacial tension at the metal–support interface.

Oxygen mobility on the support has been shown to play an important role in catalytic activity. Teichner, Zhou, Delmon, and Duprez were among the first to identify the importance of spillover oxygen for catalytic reactions involving selective oxidation.<sup>16–18</sup> Descorme and Duprez measured surface oxygen mobility on rhodium-, platinum-, and palladium-supported catalysts via temperature programmed isotopic exchange and isothermal isotopic exchange experiments in which oxygen exchange occurs via the metal catalyst particles that act as portholes for gas phase oxygen to dissociate and adsorb and then migrate to the support.<sup>19,20</sup> These authors demonstrated that both the active component and the oxide support can affect oxygen mobility. Both oxygen and hydrogen surface mobility have been found to play a role in catalytic activity. For example, Duprez found that the steam reforming of toluene over supported group 8 metal catalysts was rate limited by hydroxyl migration from the support to the metal catalytic sites.<sup>21</sup>

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**Figure 1.** TEM image of 3 wt % PdO/Al<sub>2</sub>O<sub>3</sub> (left) and 3 wt % PdO/MgO (right), together with particle size distributions. PdO is dark, and the oxide supports are lighter gray.

Our group, Ciuparu et al.,<sup>11</sup> demonstrated that oxygen from the support may contribute to the methane oxidation reaction and that this contribution is temperature dependent. Pulses of CH<sub>4</sub> plus <sup>18</sup>O<sub>2</sub> were injected over pure PdO and ZrO<sub>2</sub> supported PdO. At 325 °C, there were similar amounts of <sup>16</sup>O in the products from reaction over the pure PdO catalyst and the ZrO<sub>2</sub>-supported catalyst, suggesting little involvement of the ZrO<sub>2</sub> support. In contrast, at 425 °C, there was considerably more <sup>16</sup>O in the products from the reaction over the ZrO<sub>2</sub>-supported PdO catalyst in comparison to the pure PdO catalyst.

In a follow-up study, Ciuparu et al.<sup>22</sup> examined oxygen exchange with Al<sub>2</sub>O<sub>3</sub>- and ZrO<sub>2</sub>-supported PdO catalysts during pulsed reactant mixtures of <sup>18</sup>O<sub>2</sub> and CH<sub>4</sub> at 680 °C. Oxygen mobility on Al<sub>2</sub>O<sub>3</sub> is less than on ZrO<sub>2</sub>,<sup>20</sup> and the oxygen exchange with the Al<sub>2</sub>O<sub>3</sub> support was correspondingly lower than with the ZrO<sub>2</sub> support during reaction. On both oxide-supported catalysts, during initial methane combustion, oxygen originating from the support was preferentially observed in the products compared with oxygen supplied directly from the gas phase. Over time, as the original oxygen from the support is consumed, gas phase oxygen became a larger component of the reaction products. Oxygen exchange between the support and catalyst was postulated to be enhanced by the methane oxidation reaction.

Given that the nature of the oxide support plays a role in the methane combustion reaction over palladium at high temperature, the current study re-examines the role of the oxide support in the low temperature regime, below 350 °C where, in the absence of the methane oxidation reaction, oxygen exchange with the support is negligible.

## EXPERIMENTAL SECTION

Catalysts used in this study were 3 wt % PdO/Al<sub>2</sub>O<sub>3</sub> and 3 wt % PdO/MgO. Each catalyst was prepared by incipient wetness

impregnation with a Pd(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O precursor. Palladium nitrate dihydrate was dissolved in aqueous nitric acid (pH 1.3) and then impregnated onto the oxide supports. The materials were dried overnight at room temperature and subsequently calcined in air for 4 h at 450 °C.

**Catalyst Characterization.** The oxide supports were characterized by N<sub>2</sub> physisorption, and the catalysts were characterized by temperature programmed reduction (TPR), transmission electron microscopy (TEM), and X-ray diffraction (XRD).

Representative TEM images are shown in Figure 1, and comparative PdO TEM and XRD particle size estimates are shown in Table 1, together with N<sub>2</sub> physisorption character-

**Table 1.** Characterization Data for 3 wt % PdO/Al<sub>2</sub>O<sub>3</sub> and 3 wt % PdO/MgO, from TEM, XRD, and Physisorption Analysis

procedure	3 wt % PdO/Al <sub>2</sub> O <sub>3</sub>	3 wt % PdO/MgO
TEM average PdO particle diameter	10 ± 4 nm	12 ± 3 nm
TEM volume weighted average PdO particle diameter $d_v = \sum n_i d_i^4 / \sum n_i d_i^3$	14 ± 4 nm	15 ± 3 nm
XRD average PdO particle diameter	12 nm	13 nm
N <sub>2</sub> physisorption BET surface area of support	480 m <sup>2</sup> /g	813 m <sup>2</sup> /g
N <sub>2</sub> physisorption BJH pore volume of support	1.3 cc/g	0.82 cc/g

ization data of the oxide supports. The appropriate parameter from TEM particle size measurements for comparison with XRD crystallite particle size calculations is the volume weighted average diameter,  $d_v$ , where  $d_v = \sum n_i d_i^4 / \sum n_i d_i^3$ .<sup>23,24</sup> The XRD particle size was estimated from the Scherrer equation.<sup>25</sup> The PdO particle diameter estimates from TEM and XRD are consistent on each of the supports.

**Methane Catalytic Combustion Experiments.** Continuous flow isotopic oxygen exchange experiments were

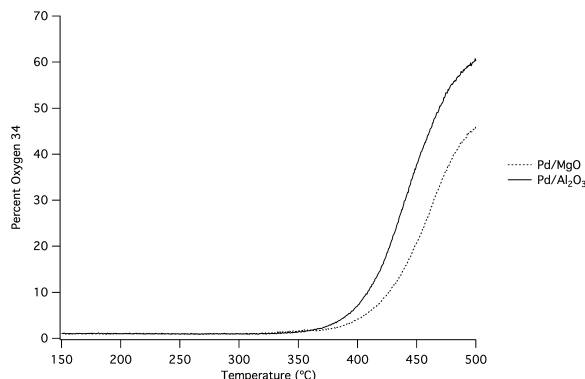
conducted using a Residual Gas Analyzer (RGA) quadrupole mass spectrometer to analyze the composition of the gas leaving the catalyst bed. Approximately 60 mg of each catalyst were loaded into a 1/4" Pyrex tubular reactor, surrounded by a ceramic radiant cylinder heater. The methane combustion experiments were conducted at 275 °C for the  $\text{Al}_2\text{O}_3$ -supported catalysts and 325 °C for the MgO-supported catalysts. The higher temperature for the MgO-supported catalyst was necessary to improve catalytic conversion during the course of the experiments. During all methane combustion experiments, the total gas flow was 50 mL/min, with an equivalence ratio of 0.5 (fuel-to-oxygen<sub>actual</sub>/fuel-to-oxygen<sub>stoichiometric</sub>).

The catalyst samples were first tested for oxygen exchange with the support in the absence of methane. We used temperature programmed isotopic oxygen exchange (TPIOE) with gas phase  $^{18}\text{O}_2$  to determine the temperature at which oxygen exchange between gas phase oxygen and the support becomes significant. The reactor temperature was ramped from 150 to 500 °C at 5 °C/min, with He flowing at 40 mL/min plus a mixture of 4%  $^{18}\text{O}_2$  in He flowing at 5 mL/min. These experiments were used to determine the temperature region in which to study the catalytic combustion of methane. We chose a temperature range where, in the absence of methane, gas phase oxygen exchange with the support is negligible.

In the second set of experiments, we prepared  $\text{Pd}^{18}\text{O}/\text{Al}_2\text{O}_3$  and  $\text{Pd}^{18}\text{O}/\text{MgO}$ . This was accomplished by first reducing the PdO to Pd metal in fresh catalyst material, and then reoxidizing the metal with  $^{18}\text{O}_2$ . To reduce PdO, 5%  $\text{H}_2$  in He flowed over the catalyst at 300 °C for one hour. Ultra-high purity He subsequently flowed for one hour to remove excess  $\text{H}_2$  from the reactor and to desorb water formed during the reduction process. The Pd metal was then reoxidized with 4%  $^{18}\text{O}_2$  in He. After this pretreatment process, the reactor temperature was adjusted to the desired value, and 1%  $\text{CH}_4$  in He was added to the existing  $^{18}\text{O}_2$  and He flow over the catalyst. The reaction gases were continuously analyzed by mass spectrometry. In these methane combustion experiments, the only significant source of  $^{16}\text{O}$  during reaction was from the oxide supports.

In the third set of experiments, we modified the catalysts to form  $\text{Pd}^{18}\text{O}/\text{Al}_2^{18}\text{O}_x^{16}\text{O}_{(3-x)}$  and  $\text{Pd}^{18}\text{O}/\text{Mg}^{18}\text{O}_x^{16}\text{O}_{(1-x)}$ . These catalysts were prepared by first reducing PdO to Pd metal by flowing He plus 5%  $\text{H}_2$  in He at 300 °C for one hour, then flowing pure He while ramping the temperature to 550 °C, and finally adding 4%  $^{18}\text{O}_2$  in He flow for two hours at 550 °C. This temperature was high enough to at least partially exchange oxygen on the supports (see Figure 2) but low enough not to cause structural changes to the catalyst such as sintering. The reactor temperature was then lowered to the desired reaction temperatures, and 1%  $\text{CH}_4$  in He was added to the existing  $^{18}\text{O}_2$  and He flow over the catalysts. The only significant source of  $^{16}\text{O}$  during reaction was from the support. In contrast with the second experiment described above, the amount of  $^{16}\text{O}_2$  available is lowered due to the partial oxygen exchange of the support with  $^{18}\text{O}$ . The purpose of this set of experiments was to determine if there is a correlation between the amount of  $^{16}\text{O}$  on the support and the amount of  $^{16}\text{O}$  initially in the reaction products.

We checked for additional possible sources of  $^{16}\text{O}$  including desorption from the walls of the reactor or the gas flow tubing, and impurities in the source gas cylinders. In all of the experimental trials, the  $^{18}\text{O}_2$  source was a cylinder of 4%  $^{18}\text{O}_2$  in He purchased from Isotec Corporation that was certified as 99% pure. We tested for the presence of  $^{16}\text{O}_2$  and  $^{16}\text{O}^{18}\text{O}$  in



**Figure 2.**  $^{18}\text{O}_2$  flow over 3 wt %  $\text{PdO}/\text{Al}_2\text{O}_3$  and 3 wt %  $\text{PdO}/\text{MgO}$  during temperature ramp. Isotopic oxygen exchange in the form of percent  $^{16}\text{O}^{18}\text{O}$  vs temperature.

our reactor during oxygen flow from this cylinder by measuring  $^{18}\text{O}_2$ ,  $^{16}\text{O}^{18}\text{O}$ , and  $^{16}\text{O}_2$  flow in an empty reactor at 275 °C. The  $^{16}\text{O}_2$  and  $^{16}\text{O}^{18}\text{O}$  attributable to impurities in the  $^{18}\text{O}_2$  cylinder levels were measured at 1% and are insignificant with respect to our experimental findings. We minimized the impact on the results from these  $^{16}\text{O}$  sources by correlating changes in the amount of  $^{16}\text{O}$  on the supports with changes in the amount of  $^{16}\text{O}$  in the reaction products.

The fourth set of experiments utilized  $\text{Pd}^{16}\text{O}/\text{Al}_2^{18}\text{O}_x^{16}\text{O}_{(3-x)}$  and  $\text{Pd}^{16}\text{O}/\text{Mg}^{18}\text{O}_x^{16}\text{O}_{(1-x)}$  as catalysts to test for  $^{18}\text{O}$  transfer from the support to the reaction products. The catalysts were prepared by first exchanging gas phase  $^{18}\text{O}_2$  with  $^{16}\text{O}$  in the catalyst samples at 550 °C, which is a high enough temperature to partially exchange oxygen on the support, as well as exchanging oxygen on PdO. The temperature was then reduced to 325 °C, and the  $\text{Pd}^{18}\text{O}$  was reduced in 5%  $\text{H}_2$  in He. The reactor was then cooled to 275 °C and the Pd metal was reoxidized with  $^{16}\text{O}_2$ , resulting in  $\text{Pd}^{16}\text{O}$  on a mixed isotope oxide support. The combustion reaction was then carried out by flowing  $\text{CH}_4$  plus  $^{16}\text{O}_2$  over the labeled catalysts at the desired reaction temperatures. In these trials, the only significant source of  $^{18}\text{O}$  was from the oxide supports.

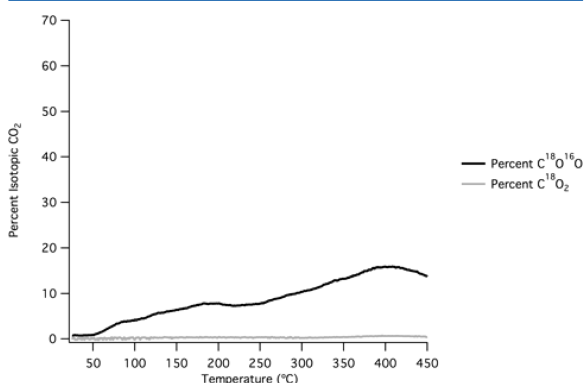
$\text{Pd}^{18}\text{O}/\text{Mg}^{16}\text{O}_x^{18}\text{O}_{(1-x)}$  was also used to investigate oxygen exchange with  $\text{C}^{16}\text{O}_2$  in the absence of methane and oxygen reactants. Temperature programmed isotopic oxygen exchange was performed between 25 and 450 °C with a temperature ramp of 8 °C/minute. The gas flow over this catalyst consisted of He flowing at 35 mL/min plus 5%  $\text{C}^{16}\text{O}_2$  in He flowing at 5 mL/min. A prior investigation by Ojala et al.<sup>26</sup> found oxygen exchange rates over  $\text{Pd}/\text{Al}_2\text{O}_3$  were higher from gas phase  $\text{CO}_2$  than from  $\text{O}_2$  at 400 °C. Our own experiment exchanging oxygen in  $\text{C}^{16}\text{O}_2$  with  $\text{Pd}^{18}\text{O}/\text{Mg}^{16}\text{O}_x^{18}\text{O}_{(1-x)}$  is used to determine the degree to which oxygen exchange between  $\text{CO}_2$  and the catalyst occurs over a wider temperature range.

## RESULTS AND DISCUSSION

**Oxygen Exchange and Methane Combustion Reactions.** Figure 2 shows the results from TPIOE exchange experiments in the absence of methane for the PdO catalysts supported on  $\gamma\text{-Al}_2\text{O}_3$  and MgO. Isotopic oxygen exchange on the  $\text{Al}_2\text{O}_3$ -supported catalyst starts to become significant around 380 °C, while exchange on the MgO-supported catalyst becomes significant around 400 °C. Pulsed TPIOE experiments were previously performed on PdO catalysts supported on  $\alpha$ -

$\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  by Ciuparu et al.,<sup>22</sup> and our results are consistent with these earlier findings. The oxygen exchange measurements shown here reveal that the maximum reaction temperature used throughout this study, 325 °C, is below the temperature at which oxygen exchange becomes significant in the absence of methane.

Figure 3 reveals that while flowing 5%  $\text{C}^{16}\text{O}_2$  in He over 3 wt %  $\text{Pd}^{18}\text{O}/\text{Mg}^{16}\text{O}_{(3-x)}$ , oxygen exchange occurs between the



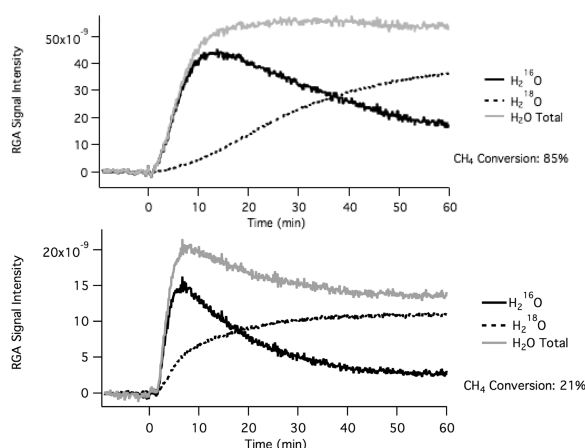
**Figure 3.** Graph of 5%  $\text{C}^{16}\text{O}_2$  in He flow over 3 wt %  $\text{Pd}^{18}\text{O}/\text{Mg}^{16}\text{O}_{(3-x)}$  during temperature ramp.

catalyst and gas phase  $\text{C}^{16}\text{O}_2$ . A comparison of the TPIOE results in Figures 2 and 3 shows greater oxygen exchange with  $\text{CO}_2$  compared to  $\text{O}_2$  at low temperatures. However, Figure 3 shows that the primary product from the  $\text{CO}_2$  oxygen exchange catalyst is single-exchanged  $\text{C}^{16}\text{O}^{18}\text{O}$ , and that double-exchanged  $\text{C}^{18}\text{O}_2$  formation is negligible in the presence of continuous  $\text{CO}_2$  flow. These results are consistent with findings by Ojala et al.,<sup>26</sup> who observed primarily single-exchanged  $\text{C}^{16}\text{O}^{18}\text{O}$  when  $\text{C}^{18}\text{O}_2$  flowed over  $\text{Pd}/\text{Al}_2^{16}\text{O}_3$  at 400 °C. The greater oxygen exchange rate for  $\text{CO}_2$  compared to  $\text{O}_2$  was attributed to the formation of carbonates on the support surface. This finding was supported by in situ FTIR spectroscopy, as well as prior studies.<sup>33,34</sup>

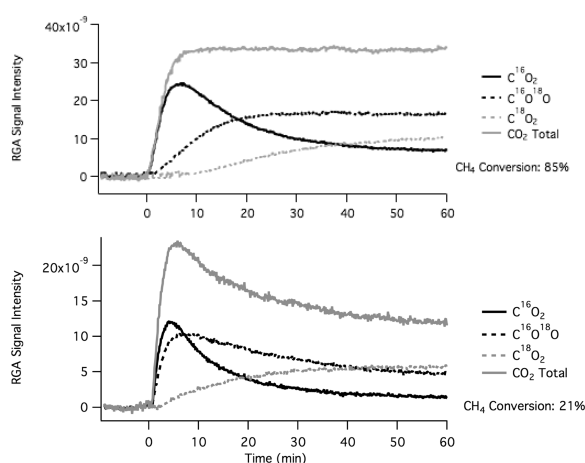
Our TPIOE results in Figure 3 show a decline in oxygen exchange at temperatures greater than 400 °C, which is due to the declining availability of  $^{18}\text{O}$  on the catalyst.

Figures 4 and 5 show normalized results from  $\text{CH}_4$  plus  $^{18}\text{O}_2$  combustion over  $\text{Pd}^{18}\text{O}/\text{Al}_2^{16}\text{O}_3$  and  $\text{Pd}^{18}\text{O}/\text{Mg}^{16}\text{O}$ . Though the only significant source of  $^{16}\text{O}$  is from the oxide supports,  $^{16}\text{O}$  is initially predominant in the water and carbon dioxide products. The percentage of  $^{16}\text{O}$  in each of these products is shown in Figure 6. The initial  $\text{CO}_2$  product is predominantly double-exchanged  $\text{C}^{16}\text{O}_2$ , showing that it does not arise from postreaction  $\text{CO}_2$  exchange of oxygen with the support. A mass balance calculation, based on the total  $^{16}\text{O}$  in the products compared to the total  $^{16}\text{O}$  in the support, indicates that about 4% of the oxygen from  $\text{Al}_2^{16}\text{O}_3$  was utilized in reaction during the 60 min period shown. We note that the support surfaces are likely saturated with hydroxyls at these conditions.

The percentage of  $^{16}\text{O}$  appearing in the  $\text{CO}_2$  product from  $\text{CH}_4$  plus  $^{18}\text{O}_2$  combustion over  $\text{Pd}^{18}\text{O}/\text{Mg}^{16}\text{O}$  at 325 °C, shown in Figure 6, ranges from about 70% at 5 min to about 30% at 60 min after start of the reaction.  $\text{CO}_2$  is initially mostly in the form of double-exchanged  $\text{C}^{16}\text{O}_2$  (see figure 5). Thus, it is not produced by the adsorption of  $\text{CO}_2$  from the gas phase and subsequent oxygen exchange with the catalyst. This is



**Figure 4.** Water distribution from  $\text{CH}_4 + ^{18}\text{O}_2$  combustion over 3 wt %  $\text{Pd}^{18}\text{O}/\text{Al}_2^{16}\text{O}_3$  at 275 °C (top) and  $\text{Pd}^{18}\text{O}/\text{Mg}^{16}\text{O}$  at 325 °C (bottom).

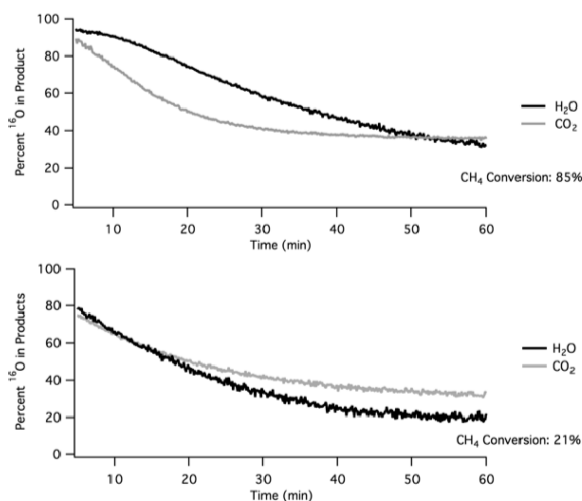


**Figure 5.** Carbon dioxide distribution from  $\text{CH}_4 + ^{18}\text{O}_2$  combustion over 3 wt %  $\text{Pd}^{18}\text{O}/\text{Al}_2^{16}\text{O}_3$  at 275 °C (top) and 3 wt %  $\text{Pd}^{18}\text{O}/\text{Mg}^{16}\text{O}$  at 325 °C (bottom).

evidenced by examining the results of pure  $\text{C}^{16}\text{O}_2$  exchange with  $\text{Pd}^{18}\text{O}/\text{Mg}^{16}\text{O}_{(1-x)}$  at 325 °C shown in Figure 3, where there is 12% conversion to  $\text{C}^{16}\text{O}^{18}\text{O}$  and almost no double-exchanged product. The high level of double-exchanged  $\text{C}^{16}\text{O}_2$  formed during methane combustion with  $^{18}\text{O}_2$  at 325 °C shown in Figure 5 indicates that most of the oxygen exchange with the support is occurring during the combustion reaction, as opposed to during readsorption of the product  $\text{CO}_2$ .

We observe that  $^{18}\text{O}_2$  from the gas phase appears more quickly in the products on the MgO-supported catalyst in comparison to the  $\text{Al}_2\text{O}_3$ -supported catalyst. A number of factors may influence the rate of gas phase oxygen utilization, including the higher reaction temperature used to study the MgO-supported catalyst (325 °C vs 275 °C), the higher surface area of the  $\text{PdO}/\text{MgO}$  catalyst on which oxygen exchange may occur (Table 1), and greater water accumulation on active sites on the  $\text{PdO}/\text{MgO}$  catalyst, as suggested by the catalytic deactivation over  $\text{PdO}/\text{MgO}$  shown in Figures 4 and 5. Catalytic deactivation is represented by the decline in total  $\text{CO}_2$  and  $\text{H}_2\text{O}$  reaction output over time. Water poisoning





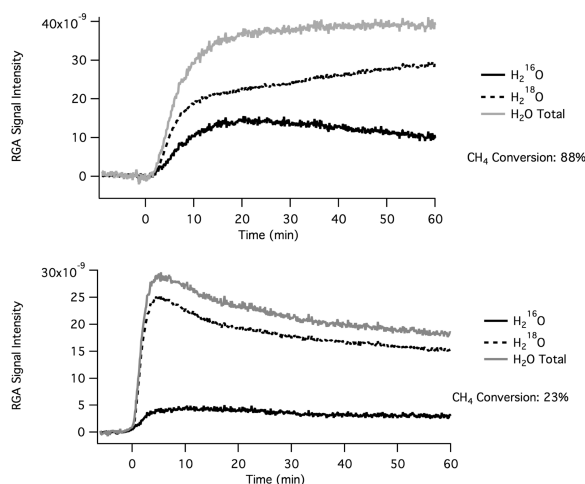
**Figure 6.** Percent  $^{16}\text{O}$  in products from  $\text{CH}_4 + ^{18}\text{O}_2$  combustion over 3 wt %  $\text{Pd}^{18}\text{O}/\text{Al}_2^{16}\text{O}_3$  at 275 °C (top) and 3 wt %  $\text{Pd}^{18}\text{O}/\text{Mg}^{16}\text{O}$  at 325 °C (bottom).

significantly decreases oxygen exchange with the support, as observed in our related work on catalytic deactivation of palladium-based catalysis.<sup>27</sup> In that study, we also observed that, in fuel lean conditions, catalytic deactivation is associated with hydroxyl accumulation and not with carbon-based deposits. Our earlier work by Ciuparu et al.<sup>22</sup> used pulses of hydrogen over Pd-based catalysts to show that hydroxyls sample the support. Another study by Ciuparu et al.<sup>35</sup> showed that  $\text{H}_2\text{O}$  is delayed in desorption compared to  $\text{CO}_2$  at temperatures below 450 °C. Taken together, these studies<sup>22,35</sup> provide additional evidence that catalytic deactivation is associated with hindered oxygen exchange between Pd and the support.

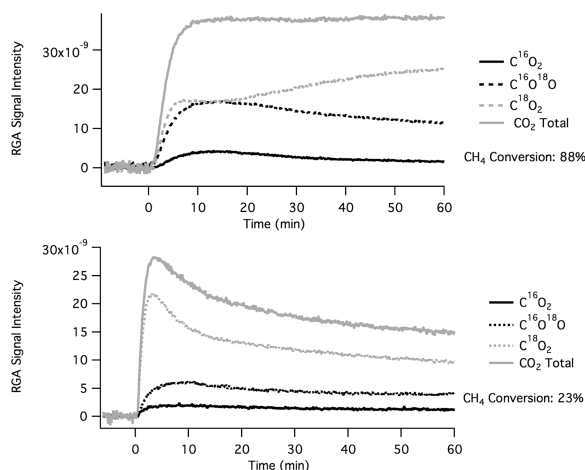
For a majority of  $\text{C}^{16}\text{O}_2$  to form on active Pd/ $\text{Pd}^{18}\text{O}$  catalytic sites at the reaction conditions illustrated in Figure 5, oxygen from the support must quickly be exchanged with oxygen on Pd during the reaction process. The water profiles shown in Figure 4 also show a predominant component of  $\text{H}_2^{16}\text{O}$  initially. Oxygen exchange with the support is fast due to hydroxyl/oxygen surface mobility and vacancies created by reaction. Hydroxyl exchange between the support and the Pd was previously shown to be faster than water desorption.<sup>22</sup>

Conversion versus time can also be seen by following the total water and  $\text{CO}_2$  profiles as a function of time. Conversion over the  $\text{Pd}^{18}\text{O}/\text{Al}_2^{16}\text{O}_3$  catalyst reaches a steady-state, as illustrated by the steady-state total  $\text{CO}_2$  concentration shown in the top section of Figure 5. In contrast, conversion over the  $\text{Pd}^{18}\text{O}/\text{Mg}^{16}\text{O}$  catalyst illustrated in the bottom section of Figure 5 shows continual decline due to catalytic deactivation. Throughout this investigation, the alumina-based catalysts demonstrated superior catalytic activity in comparison to the MgO-based catalysts.

Figures 7 and 8 show the results from  $\text{CH}_4$  plus  $^{18}\text{O}_2$  combustion over  $\text{Pd}^{18}\text{O}/\text{Al}_2^{18}\text{O}_x^{16}\text{O}_{(3-x)}$  and  $\text{Pd}^{18}\text{O}/\text{Mg}^{18}\text{O}_x^{16}\text{O}_{(1-x)}$ . We continue to observe  $^{16}\text{O}$  in the water and  $\text{CO}_2$  products but to a lesser extent than for the catalysts where the supports did not contain  $^{18}\text{O}$ . The percentage of  $^{16}\text{O}$  in the product gases originating from  $\text{Al}_2^{16}\text{O}_x^{18}\text{O}_{(3-x)}$  is calculated by mass balance to be about 2% over a one hour reaction time period. In comparable conditions, the percentage of  $^{16}\text{O}$  in the product gases originating from  $\text{Al}_2^{16}\text{O}_3$  was



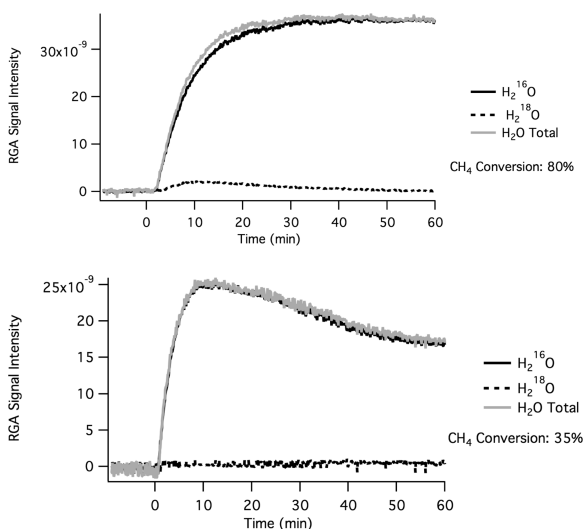
**Figure 7.** Water distribution from  $\text{CH}_4 + ^{18}\text{O}_2$  combustion over 3 wt %  $\text{Pd}^{18}\text{O}/\text{Al}_2^{18}\text{O}_x^{16}\text{O}_{(3-x)}$  at 275 °C (top) and 3 wt %  $\text{Pd}^{18}\text{O}/\text{Mg}^{18}\text{O}_x^{16}\text{O}_{(3-x)}$  at 325 °C (bottom).



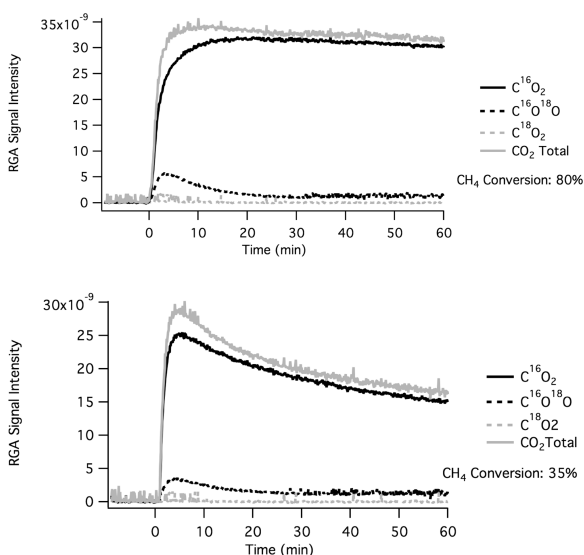
**Figure 8.** Carbon dioxide distribution from  $\text{CH}_4 + ^{18}\text{O}_2$  combustion over 3 wt %  $\text{Pd}^{18}\text{O}/\text{Al}_2^{18}\text{O}_x^{16}\text{O}_{(3-x)}$  at 275 °C (top) and 3 wt %  $\text{Pd}^{18}\text{O}/\text{Mg}^{18}\text{O}_x^{16}\text{O}_{(1-x)}$  at 325 °C (bottom).

calculated to be about 4% during combustion of  $\text{CH}_4 + ^{18}\text{O}_2$  over  $\text{Pd}^{18}\text{O}/\text{Al}^{16}\text{O}_3$ . The correlation between lower  $^{16}\text{O}$  in the support and lower  $^{16}\text{O}$  in the reaction products provides additional evidence that lattice oxygen from the support contributes heavily to the reaction products and suggests that oxygen exchange between PdO and the support surface occurs on the reaction time scale.

To provide further evidence that the catalyst supports are a source of oxygen during methane combustion, we tested  $\text{CH}_4$  plus  $^{16}\text{O}_2$  combustion over  $\text{Pd}^{16}\text{O}$ -based catalysts, where the only source of  $^{18}\text{O}$  is from the oxide supports. Figures 9 and 10 show the results from  $\text{CH}_4$  plus  $^{16}\text{O}_2$  combustion over  $\text{Pd}^{16}\text{O}/\text{Al}_2^{18}\text{O}_x^{16}\text{O}_{(3-x)}$  and  $\text{Pd}^{16}\text{O}/\text{Mg}^{18}\text{O}_x^{16}\text{O}_{(1-x)}$ . A small but significant concentration of  $^{18}\text{O}$  from the supports appears in the  $\text{CO}_2$  output, which disappears from the reaction products over time. Less  $^{18}\text{O}$  appears in the  $\text{H}_2\text{O}$  product compared to the  $\text{CO}_2$  product from reaction over the  $\text{Pd}^{16}\text{O}/\text{Al}_2^{18}\text{O}_x^{16}\text{O}_{(3-x)}$  catalyst, and the amount of isotopic oxygen in the  $\text{H}_2\text{O}$  product



**Figure 9.** Water distribution from  $\text{CH}_4 + {}^{16}\text{O}_2$  combustion over 3 wt %  $\text{Pd}^{16}\text{O}/\text{Al}_2^{18}\text{O}_x^{16}\text{O}_{(3-x)}$  at 275 °C (top) and 3 wt %  $\text{Pd}^{16}\text{O}/\text{Mg}^{18}\text{O}_x^{16}\text{O}_{(1-x)}$  at 325 °C (bottom).



**Figure 10.** Carbon dioxide distribution from  $\text{CH}_4 + {}^{16}\text{O}_2$  combustion over 3 wt %  $\text{Pd}^{16}\text{O}/\text{Al}_2^{18}\text{O}_x^{16}\text{O}_{(3-x)}$  at 275 °C (top) and 3 wt %  $\text{Pd}^{16}\text{O}/\text{Mg}^{18}\text{O}_x^{16}\text{O}_{(1-x)}$  at 325 °C (bottom).

over the  $\text{Pd}^{16}\text{O}/\text{Mg}^{18}\text{O}_x^{16}\text{O}_{(1-x)}$  catalyst is insignificant. The low to negligible concentrations of  $^{18}\text{O}$  in the products reflect the partial isotopic oxygen exchange that was achieved with our pretreatment procedure for the oxide supports, which likely occurred primarily on surface sites and not in the bulk. We were not able to quantify the amount of  $^{18}\text{O}$  remaining on the catalyst support after reducing the supported  $\text{Pd}^{18}\text{O}$  with  $\text{H}_2$  at 325 °C and subsequently reoxidizing Pd with  $^{16}\text{O}_2$  at 275 °C. That process may have left little  $^{18}\text{O}$  remaining on the catalyst support so that the support exchange consisted of mostly  $^{16}\text{O}$  with  $^{16}\text{O}$ . The lower isotopic oxygen in the  $\text{H}_2\text{O}$  output is consistent with the finding by Ciuparu et al.<sup>11</sup> that  $\text{CO}_2$  oxygen composition is reflective of the catalyst surface, while  $\text{H}_2\text{O}$

oxygen composition reflects more of the bulk due to its longer residence time on the catalyst/support.

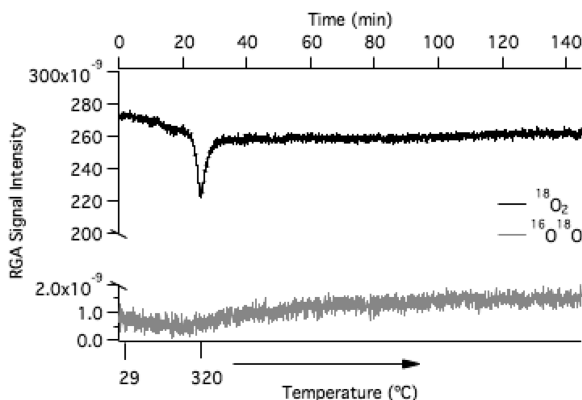
The experimental results in Figures 9 and 10 for  $\text{CH}_4 + {}^{16}\text{O}_2$  combustion show similar methane conversion levels for the 3 wt %  $\text{PdO}/\text{Al}_2\text{O}_3$  catalysts as in prior experiments, in the range of 80–88%. However, the methane conversion over the 3 wt %  $\text{PdO}/\text{MgO}$  catalysts rose from around 21% in the prior experiments to 35% in this experiment. Higher pretreatment temperatures during PdO reduction and reoxidation for this  $\text{PdO}/\text{MgO}$  sample may have increased the concentration of active catalytic sites and improved catalytic performance.

Each of the experiments described above involved catalysts where the pretreatment process included reduction of PdO in  $\text{H}_2$  followed by reoxidation with either  $^{16}\text{O}_2$  or  $^{18}\text{O}_2$ . This raised the possibility that isotopic oxygen scrambling may have occurred, which altered the distribution of isotopic oxygen bonded to Pd and to the oxide supports by hydroxyl or water migration.

Ciuparu et al. looked at the issue of scrambling during pulsed reaction mixtures of  $^{18}\text{O}_2$  plus  $\text{CH}_4$  over  $\text{PdO}/\text{ZrO}_2$  catalyst at temperatures between 323 and 423 °C.<sup>12</sup> These authors found that isotopic scrambling of oxygen atoms between reaction products and the catalyst surface did not influence the distribution of  $^{18}\text{O}$  atoms in the reaction products. Other studies have also reported an absence of isotopic oxygen scrambling between the catalyst surface and gas phase oxygen in the presence of methane in the low temperature regime.<sup>10,11</sup> In contrast, oxygen from  $\text{CO}_2$  has been shown to easily exchange with surface oxygen at temperatures below 325 °C.<sup>10,11</sup> In the absence of methane, our TPIOE experiments with  $\text{CO}_2$  (Figure 3) and experiments by Ojala<sup>26</sup> also show oxygen scrambling between  $\text{CO}_2$  and the catalyst surface at low temperature. However, oxygen scrambling in the absence of methane results in predominant formation of  $\text{C}^{16}\text{O}^{18}\text{O}$  and negligible  $\text{CO}_2$  containing two exchanged oxygen atoms. In contrast, during methane combustion, our results in Figure 5 show initially predominant  $\text{C}^{16}\text{O}_2$  formation with both oxygen atoms originating from the support. Oxygen scrambling between desorbed reaction products and the support cannot account for the oxygen distribution we observe during catalytic methane combustion, where the initial  $\text{CO}_2$  product contains predominantly double-exchanged oxygen.

To test for oxygen exchange between PdO and the catalyst support during our pretreatment process, we performed temperature programmed oxidation (TPO) of Pd metal/ $\text{Al}_2^{16}\text{O}_3$  while flowing 4%  $^{18}\text{O}_2$  in He. We ramped the temperature of the reactor from 29 to 320 °C and held the reactor at 320 °C for 2 h, while monitoring the consumption of  $^{18}\text{O}_2$  and any appearance of  $^{16}\text{O}^{18}\text{O}$ . Figure 11 reveals that, as Pd is oxidized, there is negligible appearance of  $^{16}\text{O}^{18}\text{O}$ . This indicates that there is negligible gas phase or surface oxygen exchange, consistent with the surface oxygen exchange studies by Duprez et al.<sup>19–21</sup> Even if there is minor oxygen exchange between the support and Pd–O during catalyst pretreatment, our TPO experiment shows that oxygen exchange is not appreciable. Consequently, any oxygen exchange during the synthesis process could not account for the established correlation between lower  $^{16}\text{O}$  on the support and lower  $^{16}\text{O}$  in the reaction products (e.g., comparison of Figures 7 and 4, or Figures 8 and 5 between like supports).

Other artifacts that could affect the isotopic distribution were also examined, such as residual  $^{16}\text{O}_2$  in the gas flow lines leading to the reactor. However, the quantity of  $^{16}\text{O}$  in the



**Figure 11.** Temperature programmed oxidation (TPO) over Pd/Al<sub>2</sub>O<sub>3</sub>. <sup>18</sup>O<sub>2</sub> in He flowing as catalyst is heated to 320 °C and then held at that temperature for 2 h.

reaction products over time, as illustrated in Figure 6, along with our mass balance computations that correlate the quantity of <sup>16</sup>O in the products with the quantity of <sup>16</sup>O in the support, show that the oxygen distribution is not significantly affected by the initial presence of <sup>16</sup>O<sub>2</sub>. The percentage of <sup>16</sup>O in the reaction products is between 20–40% after an hour of reaction. Figure 6 also shows that the oxygen distribution in the reaction products varies with the support. The time scale in which significant <sup>16</sup>O is found in the reaction products, together with the variation in oxygen distributions on the different supports, also suggests that the oxygen distribution is not significantly affected by the initial presence of <sup>16</sup>O in the experimental system.

Martin and Duprez<sup>20,28</sup> showed that oxygen from the gas phase exchanges with bare Al<sub>2</sub>O<sub>3</sub> starting at about 450 °C with a maximum around 620 °C and that the temperature region for oxygen exchange is lowered with the addition of metal catalyst. (See Table 2.) This was in the absence of methane.

**Table 2.** Summary of Binding Energies of Al–O and Mg–O and Activation Energies for Oxygen Exchange on the Surface of Al<sub>2</sub>O<sub>3</sub> and MgO<sup>a</sup>

	Al–O	Mg–O
binding energy	485 kJ/mol	377 kJ/mol
activation energy for oxygen exchange	125 kJ/mol	166 kJ/mol
activation energy for oxygen exchange after the addition of Pd/PdO (in the absence of methane)	27 kJ/mol	39 kJ/mol

<sup>a</sup>Binding energies are from Darwent,<sup>29</sup> and activation energies are from Martin and Duprez.<sup>20,28</sup>

Ciuparu et al. showed that the presence of methane plus oxygen significantly facilitates oxygen exchange over PdO catalyst supported on Al<sub>2</sub>O<sub>3</sub> in comparison to oxygen exchange in the absence of methane.<sup>22</sup> In a related prior study, the catalytic combustion mechanism was found to be consistent with a Mars and Van Krevelen redox reaction involving primarily a single oxygen species that bonded to two Pd atoms.<sup>11</sup>

Our results are consistent with a combination of each of these processes, where surface oxygen is utilized in reaction with methane, and with our excess oxygen reaction conditions,

reduced Pd is reoxidized with oxygen primarily from the support. Since the initial reaction products are composed primarily from oxygen exchanged with the support, oxygen exchange between the support and Pd/PdO active catalytic sites is fast, on the time scale of the surface reaction, under our reaction conditions.

Though oxygen exchange with the support surface is fast under our reaction conditions, exchange with the support bulk is expected to be slow and negligible since the binding energies in the metal oxide supports are very strong. The Al–O binding energy is around 485 kJ/mol, and the Mg–O binding energy is around 377 kJ/mol.<sup>29</sup> However, the energy barrier for oxygen migration on the surface is much smaller, and it is through oxygen surface diffusion that oxygen exchange likely occurs. At temperatures up to about 620 °C, Martin and Duprez found activation energies of oxygen exchange of 125 and 166 kJ/mol on Al<sub>2</sub>O<sub>3</sub> and MgO, respectively.<sup>20,28</sup> When Pd is added to Al<sub>2</sub>O<sub>3</sub> and MgO, and in the presence of oxygen spillover from Pd to these supports, the activation energy for oxygen exchange is further reduced to 27 and 39 kJ/mol, respectively.<sup>20,28</sup> The lower activation energy associated with Pd may be due to O<sub>2</sub> dissociation on Pd, which facilitates oxygen exchange with the support. It should be reiterated that these experiments were carried out in the absence of methane. With methane present, increased oxygen exchange has been observed.<sup>22</sup> This is expected due to the formation of oxygen vacancies on the PdO produced by the redox reaction. Table 2 provides a summary of these binding and activation energies.

The actual exchange process most likely occurs at surface defect sites such as oxygen vacancies on the support and on the PdO. A certain proportion of defect sites are thermodynamically favored in all crystals.<sup>30</sup>

The dissociative adsorption of O<sub>2</sub> onto Pd/PdO and its ultimate utilization in the methane combustion reaction are consistent with the reaction mechanisms described by Fujimoto et al.,<sup>9</sup> Au-Yeung et al.,<sup>10</sup> and Sidwell et al.,<sup>31</sup> adding that, at our reaction conditions, oxygen exchange with the support is fast. We would not observe exchanged oxygen in the reaction products without first creating dissociated oxygen atoms on the catalyst surface and exchange with the support. This is consistent with the dramatic decrease in the activation energy for oxygen exchange with the support in the presence of Pd/PdO as observed by Martin and Duprez<sup>20,28</sup> (see Table 2) and the observation by Ciuparu et al.<sup>22</sup> that this is further favored by methane reaction.

Au-Yeung et al.<sup>10</sup> examined a methane combustion reaction over 7.9 wt % PdO/ZrO<sub>2</sub>, where the reactants were 1% CH<sub>4</sub>, 2% <sup>18</sup>O<sub>2</sub>, and 2% <sup>16</sup>O<sub>2</sub> in He. The authors reported the isotopic oxygen distribution in CO<sub>2</sub> product from this reaction as a function of temperature. Their results also support the proposed van Krevelen reaction mechanism, illustrating that PdO reduction and reoxidation must be a component of the reaction process. From the figures provided in the Au-Yeung study,<sup>10</sup> we analyzed the amount of excess <sup>16</sup>O in the CO<sub>2</sub> product over the 50% <sup>16</sup>O in the gas phase reactant stream. We estimate that, even if the 7.9% PdO/ZrO<sub>2</sub> catalyst was 100% Pd<sup>16</sup>O and all the oxygen from the PdO was used to form CO<sub>2</sub> and H<sub>2</sub>O during methane combustion, there is sufficient excess <sup>16</sup>O in the CO<sub>2</sub> product to suggest <sup>16</sup>O is also supplied from the Zr<sup>16</sup>O<sub>2</sub> support.

In the fuel lean, low temperature regime under which our experiments were conducted, the rate limiting step has been identified as water desorption from the catalyst surface.<sup>3,9,32</sup> At



higher temperatures above 450 °C, the rate limiting step is methane activation where CH<sub>4</sub> decomposes to CH<sub>3</sub> + OH while breaking a Pd–O bond.<sup>3,9,32</sup> Oxygen surface mobility is faster than these rate limiting steps and therefore does not impact the observed combustion rate. Consistent with water desorption being the rate limiting step in the low temperature region, water addition significantly lowers the oxygen exchange.

Thus, our results are consistent with the literature in terms of kinetics and oxygen utilization from the catalyst and suggest that, in the low temperature range the we examined, oxygen exchange with the support can play a major role in reactivity.

## CONCLUDING REMARKS

The mechanism for catalytic combustion of methane over PdO/Al<sub>2</sub>O<sub>3</sub> and PdO/MgO in the low temperature fuel lean regime below 350 °C includes oxygen migration and exchange with the surface of the oxide support. Our results are consistent with a reaction mechanism whereby oxygen bonded to Pd is utilized in reaction and is significantly exchanged with the support. The degree of oxygen exchange with the support during reaction is dependent on temperature and the type of oxide support.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: bill.schwartz@yale.edu.

### Notes

The authors declare no competing financial interest.

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