Journal of Catalysis **203,** 64–74 (2001)
doi:10.1006/jcat.2001.3331, available online at http://www.idealibrary.com on IDEAL®

Contributions of Lattice Oxygen in Methane Combustion over PdO-Based Catalysts

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Received December 4, 2000; accepted July 1, 2001

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. The first reaction pulse at each temperature resulted in both CO_2 and water containing primarily ^{16}O. As the $^{18}O_2$ uptake from the gas phase 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 reduction titration experiments carried out after the reaction sequences. 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 isotopic composition of the surface. The behavior of the zirconia-supported catalyst was similar to that of the bulk PdO at the lowest temperature; however, as the temperature was increased above 600 K, 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 the zirconia-supported catalyst. Under these conditions the gas phase oxygen exchange with the catalyst is limited by the methane oxidation surface reaction. © 2001 Academic Press

Key Words: **palladium oxide; methane combustion; oxygen exchange; surface oxygen.**

INTRODUCTION

Palladium-based catalysts are largely accepted as the most effective catalytic systems for the methane combustion reaction. Despite extensive study under 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 the 473–923 K temperature range).

Early pulsed reaction studies by Müller *et al.* (1) employed zirconia-supported PdO catalysts labeled with $Pd^{18}O$, prepared from amorphous Pd–Zr alloys. These authors proposed that, at both 573 and 773 K, 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 largely controlled by a redox mechanism involving lattice oxygen.

Based on turnover rate measurements of the methane combustion reaction performed over zirconia-supported catalysts, Fujimoto *et al.* (3) proposed a set of elementary steps describing the reaction mechanism. In the proposed mechanism, the catalytic site is considered to be a surface oxygen vacancy or a 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 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)" (4). The authors claimed 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 (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 $Pd^{16}O$ particles using continuous flow of a reaction mixture containing $^{16}O_2$ and $^{18}O_2$ in equal amounts in

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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, but the mechanism used to discuss the data suggests that dissociation of adsorbed molecular oxygen is rate determining as the first irreversible step in a reaction series.

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 $^{18}O_2$, measuring the ^{18}O 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 10 nm (7). The reaction mixtures used consisted of 1% methane, 4% oxygen, and helium balance. The one containing regular $^{16}O_2$ was provided by Airgas, while the one labeled with $^{18}O_2$(>97%) was obtained from Isotec.

The reactivity tests were performed in a fixed-bed alumina tubular reactor with a 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 a methanizer and a FID (Flame ionization detector) that allowed measurement of the CO, CO_2, and CH_4 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 labeled oxygen atoms among the combustion reaction products, carbon dioxide ($C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$) and water ($H_2{}^{16}O$ and $H_2{}^{18}O$), as well as in the unreacted oxygen ($^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$).

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 823 K. 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 745 K. A typical run consisted of two series of 17 labeled reaction mixture pulses (0.5 ml) injected over the fully oxidized and activated $Pd^{16}O$ at constant temperature, followed by reduction with either diluted hydrogen (5% H_2 in helium) or diluted methane (0.916% CH_4 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 s. The time break between the pulse series was about 250 s. After the pulsed reduction with either methane or hydrogen, the catalyst was flushed with 5% hydrogen in helium at the same temperature for 30 min to ensure the total reduction before reoxidation with $^{16}O_2$.

For the tests with the zirconia-supported PdO, 9 mg of fresh catalyst was loaded in the reactor. Before and after the first test, the catalyst was cycled between room temperature (RT) and 1173 K under continuous flow of regular reaction mixture at a heating/cooling rate of 5 K/min in order to ensure a constant activity of the catalyst, as discussed elsewhere (7). On cooling down, the ramp was stopped at 700 K for the first test or 600 K for the second one 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 using the same time interval as for the unsupported particles. This was 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 min. 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 from those recorded initially. The sequences of runs are summarized in Table 1.

Because the catalyst is under flowing He (containing <1 ppm of oxygen as stated in the manufacturer catalog) between pulses at temperatures below 750 K, we checked whether the catalyst could become partially reduced under these conditions. To this end, a catalyst sample having a stabilized activity was held under flowing helium for 45 h at 735 K. Series of pulses were injected after 16, 23, 39, and 45 h. The average methane conversion observed with reaction mixture pulses decreased from 84 to 80% after 16 h, to 79% after 23 h, to 71% after 39 h, and to 70% after 45 h. This decrease is similar to that of similar aging under continuous reaction conditions and is therefore attributed to

TABLE 1

Sequences of Experimental Runs

		Sequence						
Catalyst	Test no.	1	2	3	4	5	6	7
Unsupported $Pd^{16}O$ particles	1	M/a [739 K]	A/c [743 K]	LRM/p [600 K]	LRM/p [600 K]	H/p [600 K]	Total reduction	o/n O [823 K]
	2	M/a [739 K]	A/c [743 K]	LRM/p [700 K]	LRM/p [700 K]	H/p [700 K]	Total reduction	o/n O [823 K]
	3	M/a [739 K]	A/c [743 K]	LRM/p [670 K]	LRM/p [670 K]	H/p [670]	Total reduction	o/n O [823 K]
	4	M/a [739 K]	A/c [745 K]	LRM/p [665 K]	LRM/p [665 K]	DM/p [665 K]	Total reduction	o/n O [823 K]
	5	M/a [739 K]	A/c [745 K]	LRM/p [625 K]	LRM/p [625 K]	DM/p [625 K]	Total reduction	o/n O [823 K]
	6	M/a [739 K]	A/c [744 K]	LRM/p [745 K]	LRM/p [745 K]	DM/p [745 K]	Total reduction	o/n O [823 K]
Zirconia-supported $Pd^{16}O$	7	LRM/p [600 K]	LRM/p [600 K]	DM/p [600 K]	Total reduction	Cycling to 1173 K		
	8	LRM/p [700 K]	LRM/p [700 K]	DM/p [700 K]	Total reduction	Cycling to 1173 K		

Note. M/a, catalyst activation with methane pulses; A/c, activity check with reaction mixture pulses ($CH_4 : {}^{16}O_2 : He = 1:4:95$); LRM/p, labeled reaction mixture pulses ($CH_4 : {}^{18}O_2 : He = 1:4:95$); H/p, reduction with 5% H_2 in He pulses; o/n O, treatment under flowing ${}^{16}O_2$ overnight; DM/p, diluted methane (0.916% of methane in He) pulses for catalyst reduction. Total reduction was performed with a continuous flow of 5% of hydrogen in He for 30 min at the test temperature. Cycling was performed at 5 K/min heating/cooling rate under flowing of unlabeled reaction mixture. The values in square brackets are the temperatures for each sequence.

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, 0.5, and 0.021 ml) of reaction mixture injected over the catalysts at a 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.

In all of the experiments reported here 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 mass spectrometry analysis; the carbon material balance and conversion were determined from gas chromatographic analysis. Therefore, in the mass selective detector, samples were analyzed for ions with masses 17 and 19 for water; masses 32, 34, and 36 for oxygen; and masses 44, 46, and 48 for carbon dioxide isotopomers.

RESULTS

In the presence of reaction products, oxygen exchange between the gas phase and the surface was found to be irreversible and limited by the methane oxidation reaction. The distribution of oxygen isotopomers for all investigated temperatures was similar to the one depicted in Fig. 1 and showed no significant oxygen scrambling between surface and gas phase oxygen, in agreement with previous results (1, 2).

The first set of runs (tests 1 to 6 in Table 1) was carried out for an unsupported bulk PdO catalyst. The distribution of

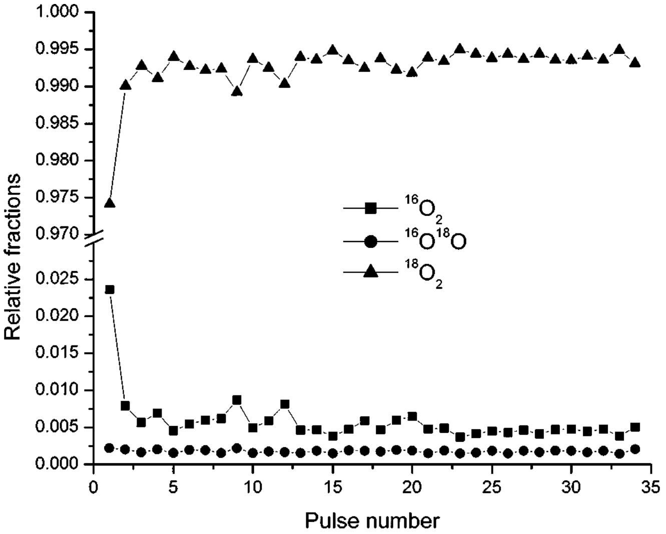

FIG. 1. Typical distribution of oxygen isotopomers following labeled reaction mixture pulses over unsupported $Pd^{16}O$ particles.

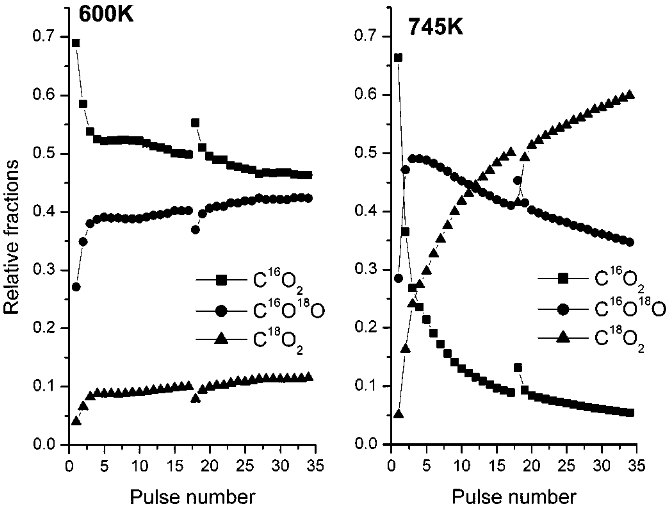

FIG. 2. Distribution of carbon dioxide isotopomers observed with labeled reaction mixture pulses injected over the unsupported $Pd^{16}O$ particles at 600 and 745 K.

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 Fig. 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 Fig. 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 that oxygen already at the surface is predominantly used for methane combustion. Except for the lowest temperature (600 K), 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 17 (see Fig. 2) produced a slight increase in the relative fraction of $C^{16}O_2$ at all reaction temperatures. This increase is rapidly lost and is due to an increase of surface ^{16}O concentration caused by bulk oxygen migration toward 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 Fig. 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 becomes limited by exchange with the bulk at high temperatures.

Figure 4 shows the relative distribution of the water isotopomers for three temperatures as a function of pulse number (Fig. 4a) and as observed for the water produced with the last pulse of the series at different temperatures (Fig. 4b). As expected, the concentration of $H_2{}^{18}O$ increased as the pulse number increased and as the temperature increased. The isotopic composition of water resulting from methane combustion over the $Pd^{16}O$ 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.

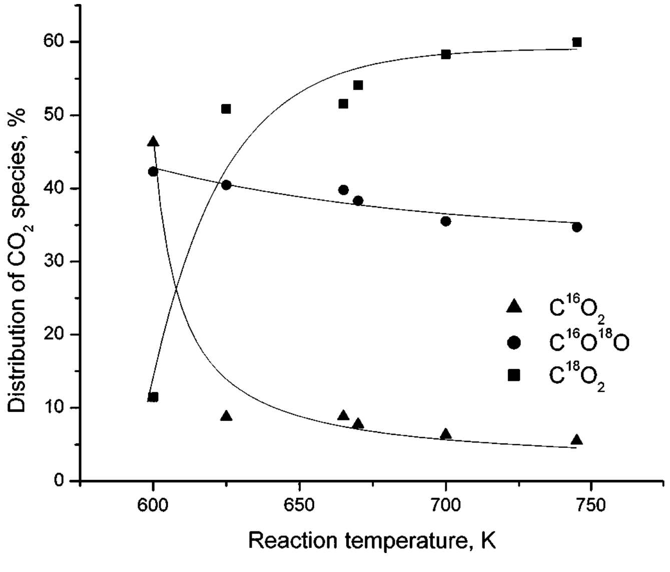

FIG. 3. Distribution of carbon dioxide isotopomers resulting from the last pulse of the second series of labeled reaction mixture pulses injected over unsupported $Pd^{16}O$ particles at different temperatures.

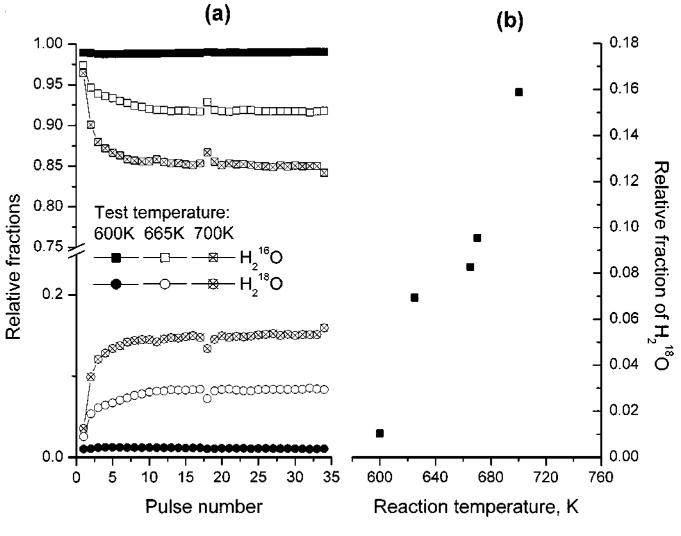

FIG. 4. Distribution of water isotopomers observed for labeled reaction mixture pulses injected over unsupported $Pd^{16}O$ particles at different temperatures (a) and the relative fractions of $H_2{}^{18}O$ determined for the last reaction mixture pulse at the reaction temperatures used (b).

To determine both the overall oxygen exchange and to qualitatively assess the distribution of oxygen isotopes as a function of radial position inside the particles, the catalyst was reduced after reaction at the reaction temperature using pulses of either diluted methane or diluted hydrogen. The relative fractions of water isotopomers resulting from catalyst reduction at different temperatures are given in Fig. 5. Examination of the plots in Fig. 5 reveals 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 in the $H_2{}^{18}O$ concentration in the 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 that the composition of water resulting from the reaction reflects the bulk composition of the catalyst particle. For reduction with diluted methane (665 and 745 K), 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 (600, 625, 670, and 700 K). For the above reasons Fig. 5 is presented as the distribution of isotopomers versus the percentage of the catalyst reduced.

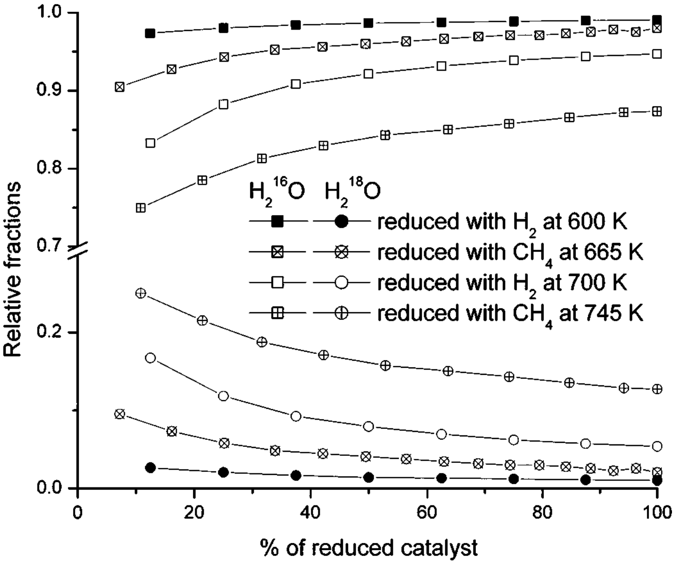

FIG. 5. Distribution of water isotopomers at different stages of PdO reduction using hydrogen (600 and 700 K) or methane (665 and 745 K). Reduction was performed at the same temperature as that of the reaction.

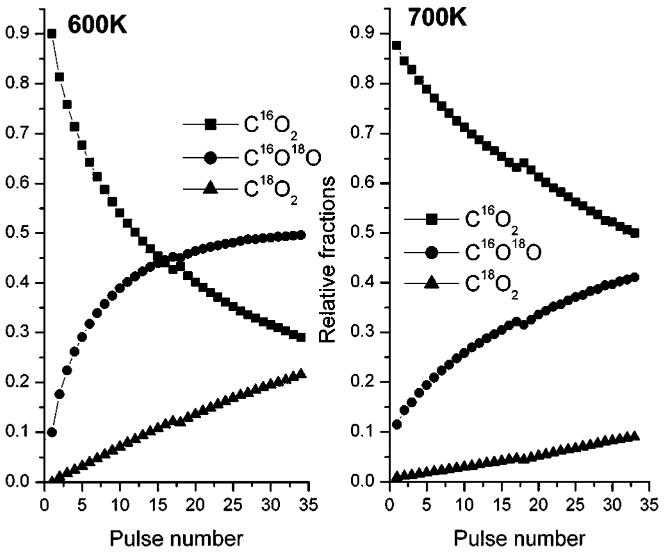

FIG. 6. Distribution of carbon dioxide isotopomers observed following labeled reaction mixture pulses injected over zirconia-supported $Pd^{16}O$ particles at 600 and 700 K.

For the next series of experiments the zirconia-supported catalyst was used. The zirconia-supported catalyst behaved similarly to the unsupported PdO catalyst at the lowest temperature of these experiments (600 K). However, the distributions of carbon dioxide isotopomers plotted as a function of pulse number in Fig. 6 show significant differences from the unsupported PdO at the higher temperature. The most important feature is that the amount of ^{16}O in the reaction products increases considerably with temperature for similar amounts of methane converted. From the ^{16}O mass balance, 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, consistent with our data following the temperature dependence observed by Duprez and Martin (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 Fig. 7. Again, the ^{18}O-containing isotopomer is more abundant at the lower temperature (600 K) with a slightly higher rate of ^{18}O penetration into the bulk compared to the unsupported PdO, consistent with smaller particle size. At this temperature oxygen exchange between the support and the PdO particles was found to be slow compared to exchange from the gas phase. At the higher temperature (open symbols in Fig. 7) the fraction of labeled oxygen in the water is lower than that at 600 K and increases much slower with pulse number, again consistent with the observation that oxygen

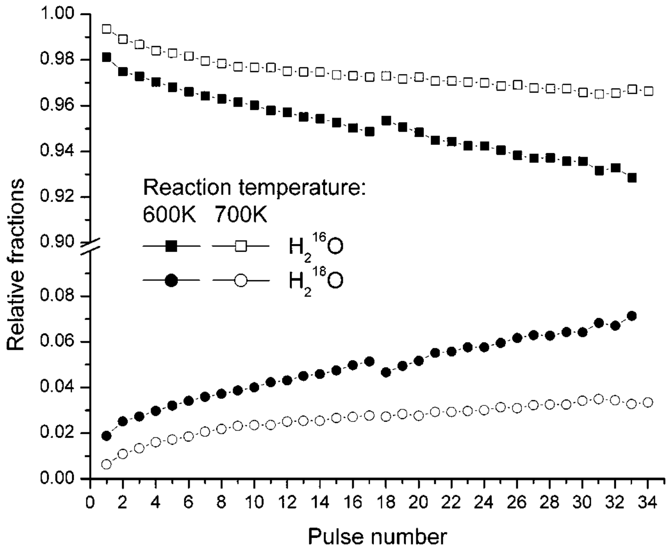

FIG. 7. Distribution of water isotopomers observed following labeled reaction mixture pulses injected over zirconia-supported $Pd^{16}O$ particles at different reaction temperatures.

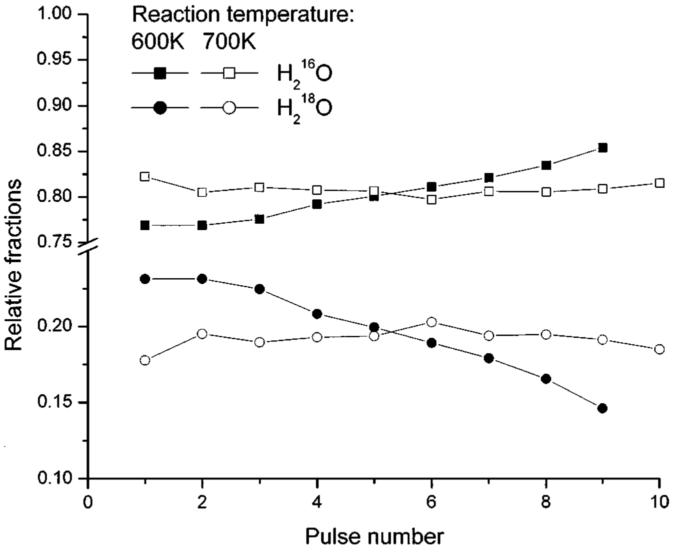

FIG. 9. Distribution of water isotopomers during the reduction of the supported catalyst using diluted methane pulses after labeled reaction mixture pulses injected at different temperatures.

exchange with the support is faster than exchange with the gas phase.

The isotopic distribution for carbon dioxide and water resulting from reduction experiments performed with diluted methane are given in Figs. 8 and 9, respectively. At 600 K the first reduction pulse gave ^{18}O-rich reaction products suggesting that 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 700 K 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 700 K the isotopic composition of the reaction products changes insignificantly.

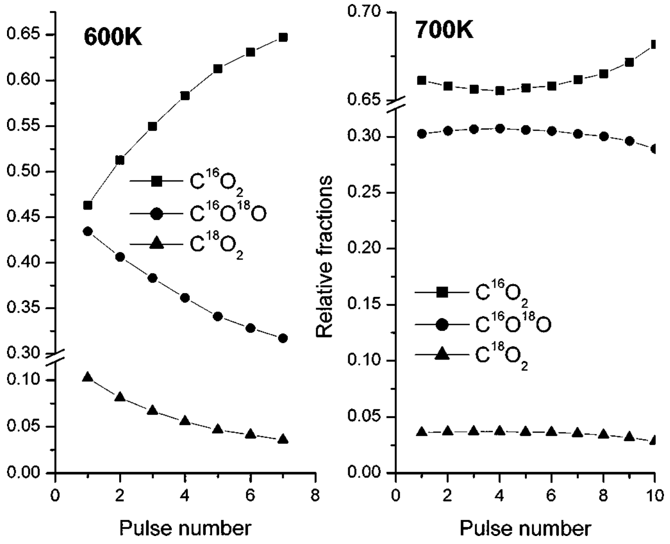

FIG. 8. Distribution of carbon dioxide isotopomers observed during the reduction of the zirconia-supported catalyst with diluted methane pulses after labeled reaction mixture pulses at 600 and 700 K.

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 Müller's study is significantly higher than the number 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, readsorption 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 PdO_x during methane oxidation (4). Vacancy development, however, especially under conditions where water is desorbed between pulses (pulsed experiments above 725 K), would be expected to be a negative order with respect to oxygen. If vacancy development were the rate-limiting step, therefore, one would expect to see a negative order with respect to oxygen under these conditions. It should be noted that the reaction order with respect to oxygen reported by many investigators is positive and near zero. Another possible methane activation step is the dissociative adsorption of methane on a surface Pd–O pair as proposed by Broclawik *et al.* (8).

Au-Yeung *et al.* (5) used an isotopically labeled technique to investigate the methane oxidation pathways on PdO catalysts. They concluded that 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 that reoxidation is slow, consistent with the work reported here. From an estimated ^{16}O balance, however, either the bulk and the surface of PdO are partially reduced or oxygen exchange with the zirconia support plays a role under their experimental conditions; however, we observed that at 600 K—the maximum temperature used in Au-Yeung's experiments—the oxygen exchange rate with the support is low.

Based on results obtained with pulsed studies over zirconia-supported $Pd^{18}O$ catalysts prepared by oxidation of palladium–zirconia alloys, Müller 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 and, as noted earlier, due to the large number of turnovers per site, readsorption of reaction products may become important and the isotopic distributions are averaged values for a large number of surface reduction/reoxidation cycles.

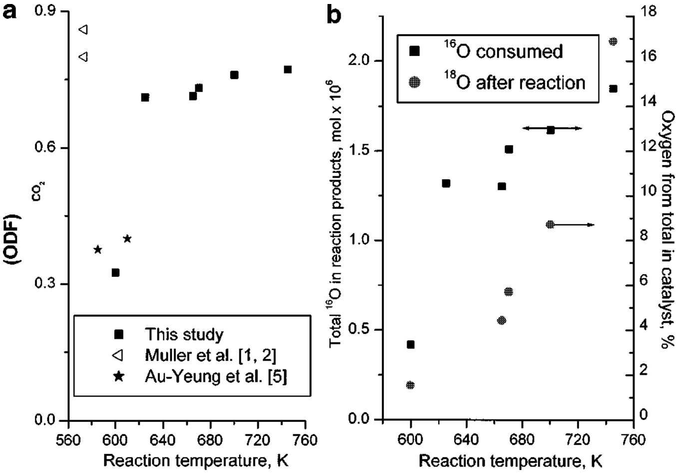

FIG. 10. The ODF values for carbon dioxide (a) and the overall lattice oxygen consumption (b) at different reaction temperatures.

For an easier evaluation of the distribution of ^{18}O in water and carbon dioxide isotopomers we introduce the gas phase oxygen distribution factor (ODF). For water, the ODF equals the relative fraction of $H_2{}^{18}O$ and for CO_2 it is computed with the equation

$$(\mathrm{ODF})_{\mathrm{CO_2}} = \frac{(A_{46} + 2A_{48})}{2(A_{44} + A_{46} + A_{48})}.$$

In Fig. 10 the values for the $(\mathrm{ODF})_{\mathrm{CO_2}}$ are presented together with the lattice oxygen consumption (computed from the material balance) as functions of the reaction temperature. Comparing the $(\mathrm{ODF})_{\mathrm{CO_2}}$ values with the similar $H_2{}^{18}O$ profile depicted in Fig. 4b one can easily observe the differences in the distribution of ^{18}O in water and carbon dioxide following labeled reaction mixture pulses. Based on this observation, one could be tempted to claim that hydrogen and carbon are oxidized following different mechanisms. However, during reduction with diluted methane pulses after reaction, the distribution of ^{18}O between water and CO_2 was approximately equal, as plotted in Fig. 11.

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). As shown in the model in Fig. 12a, 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]

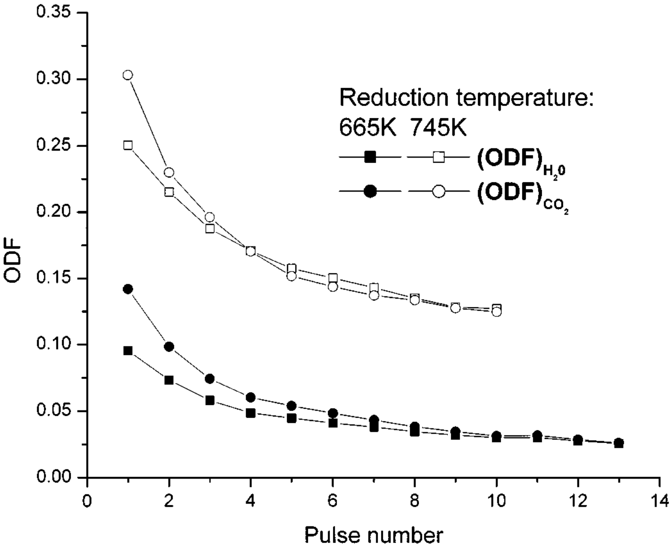

FIG. 11. The ODF values for water and carbon dioxide determined for the reduction of unsupported catalyst with diluted methane pulses.

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 Figs. 12b and 12c. 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. Not surprisingly, PdO does not occur uncomplexed in nature. 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 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

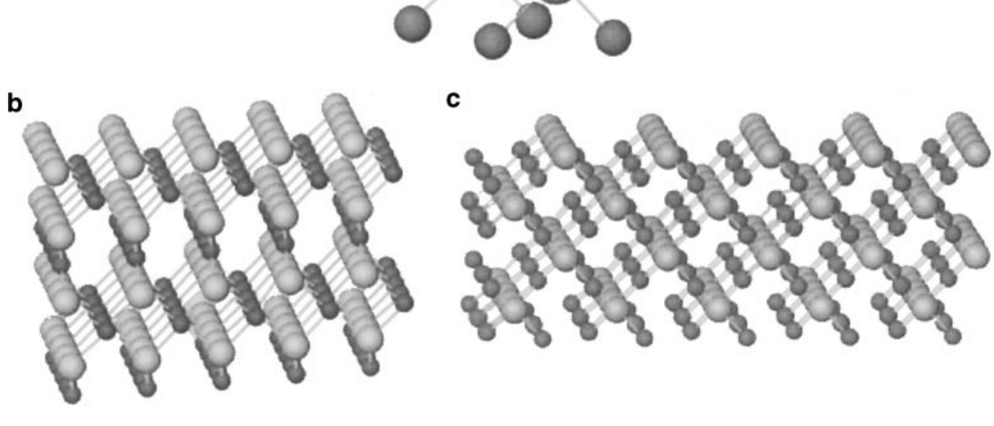

FIG. 12. Crystalline structure of PdO: (a) unit cell; (b and c) bulk terminated (001) and (110) surfaces, respectively. The dark balls represent Pd atoms and the light balls, O atoms.

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 under 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 the methane oxidation reaction, surface reoxidation/oxygen exchange with the gas phase is slow (11). Figure 5 shows low ^{18}O uptake, especially at low temperatures, and Fig. 10b 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 under transient conditions the surface can consist of a patchy array of phases (12). This observation is also consistent with the previous TPD and STM results of Zheng and Altman (13) 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 surface tensions lower than those of 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 toward the surface, thus equilibrating the concentration of the vacancies between surface and bulk. This is consistent with our experimental observation that, under 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 types of surface oxygen species. The starting point in explaining this behavior is to identify the processes determining the isotopic composition of the PdO surface.

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, independent of 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 ^{16}O from the bulk of the catalyst. For supported catalysts oxygen exchange from the support can also play a role. The following discussion is for the unsupported PdO; additional considerations for supported systems follow this discussion.

It should be noted here that the ^{16}O/^{18}O ratio at the catalyst surface is determined by the competition between reoxidation processes. Reoxidation from the gas phase is an activated process (14) 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 600 K, 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 Fig. 10b. The uptake of gas phase oxygen also meets the expected evolution. The postreaction reduction experiments showed a small increase in the ^{18}O uptake at low temperatures and a step increase between 700 and 745 K.

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 interrelated 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-s time interval between two consecutive pulses. This is reflected in the low concentration of ^{18}O-containing isotopomers observed during reaction at 600 K. 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 4-min pause after the 17th pulse (see Fig. 2) when the catalyst was exposed only to He ($O_2 < 1$ ppm).

The hydroxyls produced by reaction have a long residence time on the catalyst at temperatures below 725 K (15) and the hydrogen effectively samples the bulk. The isotopic oxygen distribution in water reflects that of the bulk (as determined 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 the 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 600 K. This is consistent with our previously reported results (15) showing that water desorption lags significantly behind the carbon dioxide desorption. At temperatures above 600 K, however, surface oxygen exchange becomes faster than exchange with the bulk and gradients develop in the particle. At 745 K 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 that of hydroxyl desorption. This is consistent with our finding at these temperatures and pulse conditions that CO_2 desorption significantly precedes water.

Along these lines, a reaction mechanism consistent with the experimental results presented here can be summarized by 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 the 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 (<600 K) for our reaction system the oxygen exchange between the PdO phase and the support is slow.

During reduction with methane at 700 K the oxygen transfer from the support to reoxidize the PdO particles causes the reduction of the support. Under reaction conditions where the rate of oxygen exchange between PdO and support is higher than the rate of bulk oxygen diffusion, or the rate of oxygen exchange with the gas phase; the isotopic composition of the CO_2 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 catalysts showed that the reaction mechanism is not influenced by the support. However, the support significantly contributes to the oxygen pool of the catalyst. This explains the good results for ceria and 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 unsupported and zirconia-supported $Pd^{16}O$ particles to investigate the contribution of the lattice oxygen in the reaction mechanism of methane combustion. Several conclusions derived from the results are 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. Under our experimental conditions the reactivity data shows that this one form of oxygen is responsible for the oxidation of both 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 745 K, 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 700 K the exchange of oxygen between support and PdO is very rapid.

ACKNOWLEDGMENTS

We acknowledge with pleasure the support of this work by the Department of Energy, Division of Chemical Sciences, Grant DE-FG02-96ER14679. The authors are also thankful to the Petroleum Research Fund–American Chemical Society for support under the Grant 34181-AC5.

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