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Contributions of lattice oxygen to the overall oxygen balance during methane combustion over PdO-based catalysts

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Abstract

The methane combustion mechanism was investigated by means of pulsed reaction experiments using a reaction mixture labeled with $^{18}O_2$. The catalysts employed were pure PdO, zirconia and ceria–zirconia-supported PdO particles fully oxidized with ^{16}O. Complementary continuous flow temperature programmed reaction experiments were also used.

Our results confirmed the redox combustion mechanism. Exchange of oxygen from the bulk and from the support with the surface can be faster than from gas phase. This implies steady-state bulk vacancies for conditions where exchange with the bulk is fast.

An important observation is that surface hydroxyls resulting from methane oxidation impede surface reoxidation, leading to a certain degree of catalyst deprivation of oxygen and formation of bulk oxygen vacancies. This can be responsible for the lower temperature of thermal reduction for pure PdO as compared to supported PdO particles. For the supported catalyst, oxygen vacancies in the PdO phase are refilled with oxygen from the support, consistent with the larger amounts of ^{16}O observed in the reaction products resulting from PdO on zirconia. This oxygen transfer may be responsible for the lower thermal decomposition rate of PdO particles supported on ceria–zirconia.

Keywords: Palladium oxide; Methane combustion; Water inhibition; Oxygen vacancies

1. Introduction

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

Under reaction conditions where the crystalline PdO is stable, many authors suggest a redox or Mars and van Krevelen type of mechanism. Early studies on a labeled $Pd^{18}O$ catalyst prepared from a glassy Pd–Zr alloy reported by Muller et al. [1] concluded that the combustion reaction proceeds partly via a redox mechanism. They proposed differences in the oxidation mechanisms of hydrogen and carbon. In a more recent and similar study employing the same catalyst [2] these authors proposed two potential explanations for the differences observed in the relative amounts of labeled CO_2 and labeled water, respectively: either differences in the scrambling properties of the respective molecules, or a different contribution of a redox mechanism to the formation of the respective product species. The difference in reaction mechanisms consists in “the abstraction of hydrogen from adsorbed methane species is a normal surface reaction, whereas

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the formation of oxygen–carbon bonds is more pronounced subjected to a redox mechanism" [2].

Fujimoto et al. [3] proposed a set of elementary steps for the reaction mechanism 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 Mars and van Krevelen and avoids the need for the co-existence of a separate Pd metal phase in atomic contact with PdO_x during methane oxidation [4]. Au-Yeung et al. [5] used an isotopically labeled technique to investigate the methane oxidation pathways on PdO catalysts. They concluded the lattice ^{16}O in PdO is more efficiently used in methane combustion than labeled ^{18}O atoms from the gas phase and their results suggested reoxidation of the catalyst with O_2 from the gas phase is slow.

In a recent study, we also observed important differences in distribution of labeled oxygen atoms in reaction products [6]. We showed that the (0 0 1) and (1 1 0) bulk-terminated surfaces—PdO surfaces with the lowest energies, expose only a single type of oxygen species, that is oxygen atoms bridge bound to two Pd atoms. Charge compensated surfaces can be created by removing half the oxygen atoms from the bulk-terminated surfaces. Although this creates an ordered array of surface oxygen vacancies, the surface is fully oxidized in that all the surface Pd atoms are in formal +2 oxidation state. As a result, oxygen cannot absorb at the vacancies without oxidizing the surface Pd atoms beyond the +2 oxidation state. Similarly, 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+} [6]. This approach makes the possibility of different mechanisms for oxidation of carbon and hydrogen atoms from the methane molecule at the PdO surface unlikely.

We [7] demonstrated that water remains longer at the surface, as compared to CO_2, explaining the differences observed in the distribution of labeled oxygen between the two reaction products [6]. The isotopic distribution of water produced was found to be reflective of the bulk composition, in contrast to the isotopic composition of the CO_2 produced, which was found to reflect the instantaneous isotopic composition of the surface. We also proposed that the presence of water at the surface is responsible for the slight deprivation of oxygen of the catalyst at reaction temperatures where water inhibition is important [6].

The present work is dedicated to further investigation of the reaction mechanism and, in particular, to directly probe the role of water on the overall oxygen mass balance of the catalyst.

2. Experimental

The experimental setup employed was described in detail in the previous work [6–8]. Its key features are: (i) the combined analytical system consisting of a HP5791A quadrupole mass spectrometer and a GC with methanizer and FID, allowing simultaneous measurements of the distribution of reaction products isotopomers and determination of carbon and oxygen material balance and conversion, respectively; (ii) rapid switching between continuous flow and pulsed operation conditions; (iii) flexibility in operation; it accommodates a wide range of catalyst loadings (from few to 100 mg), flow rates, pulse frequencies, temperatures and heating rates.

Pure (99.999%) PdO powder from Aldrich and two supported PdO catalysts—zirconia and ceria–zirconia, respectively, were used as methane combustion catalysts. The preparation and characterization of the zirconia-supported catalyst have been described in detail elsewhere [9]. The ceria–zirconia-supported catalyst was prepared by wet impregnation with palladium nitrate precursor of a ceria–zirconia support prepared using the procedure described in [10], to give a catalyst with 3% metal loading. After impregnation, the catalyst was dried overnight at room temperature and subsequently calcined in flowing oxygen at 823 K. One part pure PdO powder and four parts zirconia support were mixed and ground together to give a homogeneous mechanical mixture comprising 20% PdO by weight. This mixture was used as a reference for the unsupported catalyst. Before tests, the catalyst samples were cycled once in reaction mixture (1% CH_4 and 4% O_2 in He) between 673 and 1173 K. This procedure was observed to stabilize the catalytic activity with time on stream [9].

Temperature programmed reaction (TPR) profiles were recorded for the mechanical mixture and stabilized samples of the two supported catalysts under continuous flow of reaction mixture between 673 and

1173 K at a 5 K/min heating rate. The contact time used was 0.1 s. For the isotopically labeled experiments, before each run the catalyst was fully reduced in 5% H_2 in He and then reoxidized in research grade $^{16}O_2$ flow (Airgas) overnight at 823 K. The experiments consisted of pulses (500 μl) of reaction mixture (1% CH_4 and 4% $^{18}O_2$ in He from Isotec) injected at 700 K in a He stream flowing continuously over the catalyst. After labeled pulses, the catalyst was reduced in steps to assess the ^{18}O uptake at the surface and in the bulk. For these experiments the reactor was loaded either with 3 mg of pure PdO or with 9 mg of supported catalyst containing 3% metallic palladium by weight. The PdO particle sizes determined by X-ray diffraction for catalysts with similar loadings prepared using the same method were in the range of 15–20 nm after cycling to 1173 K in reaction mixture [9]. The reactor effluent was analyzed in a gas chromatograph with FID and methanizer, which allows determining the CH_4 and CO_2 concentrations. The distribution of ^{18}O atoms in the reaction products was determined with a HP 5791A quadrupole mass selective detector.

A final experiment has been designed to study the effect of water on the gas phase oxygen uptake onto the catalyst. The reactor was loaded with 3 mg of pure PdO. The catalyst was first completely reduced with hydrogen at 575 K and then reoxidized with flowing air at 875 K for 12 h. After reoxidation, the reactor was cooled down at 700 K under flowing air. At that temperature, the reaction system was switched to pulse mode with pure He flowing continuously over the catalyst and it was completely reduced by injecting pulses of 21 μl of pure methane at time intervals of 6 min. Following the pure methane pulses, only CO_2 and water were detected. No water was detected following a pure hydrogen pulse injected after the last methane pulse showing no methane conversion, suggesting at this temperature and pulse frequency complete reduction of the catalyst with methane can be achieved. Methane conversions for each pulse were determined by gas chromatography.

A separate experiment was performed to check for the presence of carbon deposition at the surface following a similar reduction procedure. Carbon at the surface was not observed at temperatures below 825 K. These results are consistent with our earlier results showing no detectable carbon formation during partial reduction of PdO with methane [8,11].

Two sets of experiments were performed to assess the effect of water on the oxygen exchange and uptake with a partially reduced PdO catalyst in the absence of methane. Either dry helium or He with 2.45% of water were used as carriers. First, the completely oxidized catalyst, obtained as described above, was partially reduced with one pulse of 21 μl pure methane at 700 K. After partial reduction, series of 16 pulses of 500 μl of 4% $^{18}O_2$ ($<$97% isotopic purity) in He from Isotec were injected both with dry and wet He carriers at 700 K. The isotopic distribution of oxygen in the exhaust stream was determined pulse to pulse with the mass spectrometer for ions with masses 32, 34 and 36 for oxygen, and 19 for $H_2{}^{18}O$, respectively.

After the labeled oxygen pulse series, the oxygen content of the catalyst was determined by complete reduction of the catalyst with pure methane pulses of 21 μl injected in a dry helium carrier flowing continuously over the catalyst. The mass spectrometer allowed determination of the isotopic distribution of oxygen in the reaction products resulting from catalyst reduction and GC allowed determining the methane conversion.

3. Results

The TPR profiles recorded for the three catalysts are plotted in Fig. 1. They show the typical features for palladium-based catalysts. The activity increases with temperature, reaches a maximum around 975 K, and then decreases as the temperature increases showing the “negative activation” phenomenon associated with the thermal reduction of PdO. As the PdO is completely reduced to metallic palladium the activity increases again with the temperature. However, it should be noted that the temperature associated with the maximum activity is slightly different for the two supported catalysts when compared to the mechanical mixture. The mechanical mixture started losing activity at a temperature about 20 K lower than the supported PdO particles. We reported a similar observation earlier [9] and proposed a particle size effect as being responsible for this behavior. While this explanation stands, it is also possible that the mechanism by which the supports stabilize the PdO phase, as observed by us [9] and many other authors [12–14], consists of the rapid reoxidation of the PdO phase with oxygen from the support. This is consis-

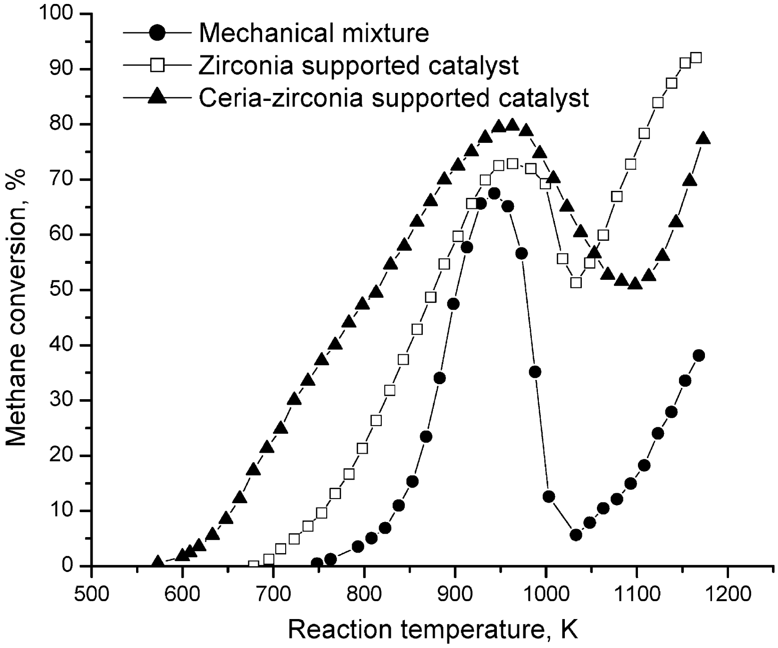

Fig. 1. Methane combustion temperature reaction profiles for different PdO-based catalysts at 5 K/min heating rate.

tent with high oxygen mobility supports decreasing the activity hysteresis gap associated with palladium reduction–reoxidation cycles and with the slower rate of activity decay during the thermal reduction of PdO observed for the ceria–zirconia-supported catalyst as compared with the zirconia-supported catalyst.

An important contribution of oxygen from the catalyst, either from the bulk of PdO grains or from the support, was observed in the isotopically labeled pulsed experiments performed at 700 K with pure PdO and zirconia-supported catalysts. The distributions of carbon dioxide and water isotopomers observed following series of labeled reaction mixture pulses of 0.5 ml injected at 80 s time interval are given in Figs. 2 and 3, respectively. It should be emphasized that the conversion did not change pulse to pulse, despite the important change observed in the distribution of isotopomers in the reaction products. Following the first pulse in the series both carbon dioxide and water showed predominantly unlabeled oxygen, suggesting lattice oxygen is used to oxidize the methane, thus reducing the catalyst—consistent with the proposed Mars and van Krevelen reaction mechanism. However, for subsequent pulses the distribution of labeled oxygen atoms in water and CO_2 produced in the reaction were significantly different. The carbon dioxide produced is rapidly enriched in labeled oxygen, while water contained predominantly unlabeled oxygen, even at large pulse numbers. This significant difference is better observed in the plots in Fig. 4 (solid symbols) showing the distribution of labeled oxygen in reaction products observed pulse to pulse for the pure PdO catalyst.

The reduction of the pure PdO catalyst performed immediately after reaction at the same temperature with pulses of 5% hydrogen in helium showed the isotopic distribution of water isotopomers depicted by the open symbols in Fig. 4. It should be noted that the first hydrogen pulse produced water having the isotopic distribution similar to that of the last pulse of reaction mixture. However, at larger pulse numbers the water resulting from the catalyst reduction is enriched in unlabeled oxygen suggesting a non-uniform distribution of the labeled oxygen into the catalyst grain. Assuming a layer-by-layer reduction, the PdO surface is richer in labeled oxygen than the bulk.

Similar pulsed methane oxidation reaction and subsequent reduction of the pure PdO catalyst at different

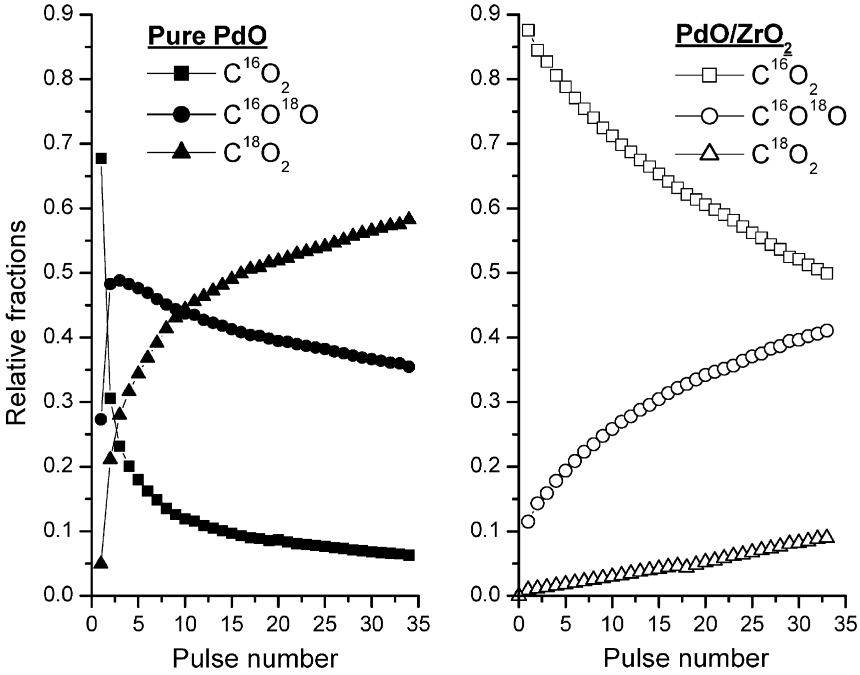

Fig. 2. Pulse to pulse distribution of CO_2 isotopomers observed in labeled pulsed methane combustion experiments at 700 K with pure PdO (solid symbols) and zirconia-supported PdO (open symbols) catalysts.

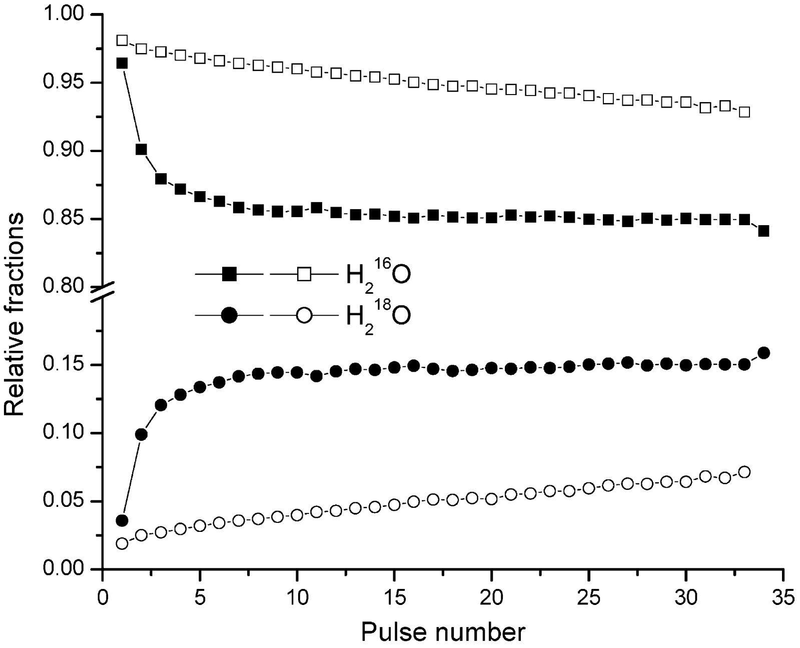

Fig. 3. Pulse to pulse distribution of H_2O isotopomers observed in labeled pulsed methane combustion experiments at 700 K with pure PdO (solid symbols) and zirconia-supported PdO (open symbols) catalysts.

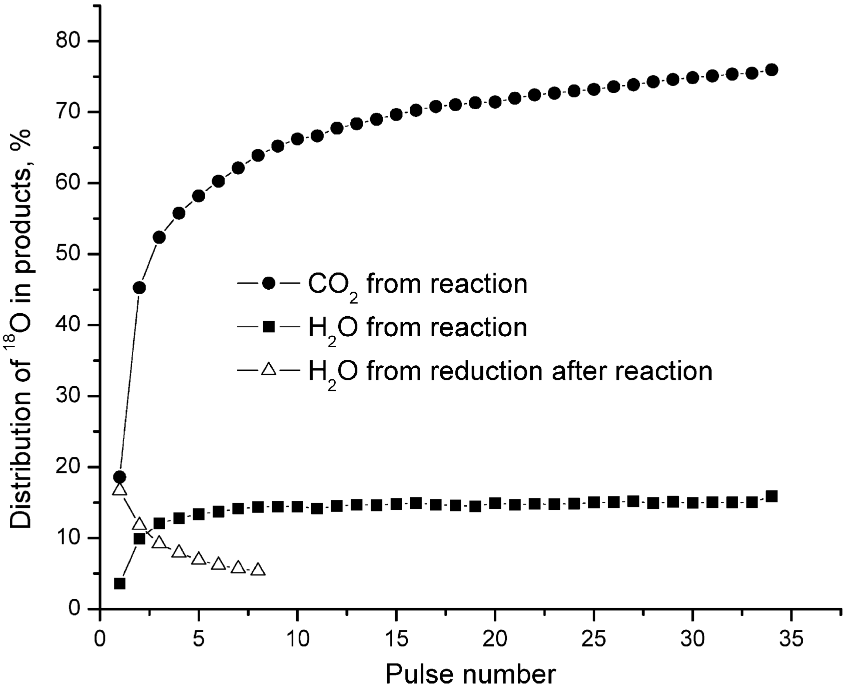

Fig. 4. Pulse to pulse, overall distribution of labeled oxygen in reaction products obtained at 700 K during pulsed reaction (solid symbols) and pulsed reduction (open symbols) of the pure PdO catalyst after reaction.

temperatures were reported elsewhere [6]. The overall oxygen material balance from these experiments clearly showed that, for pulsed methane combustion experiments performed at temperatures between 600 and 750 K, steady-state bulk vacancies are present in the pure PdO catalyst. We proposed that water may be responsible for blocking the oxygen uptake from the gas phase and that refilling of surface oxygen vacancies from the bulk may be more rapid than reoxidation from the gas phase.

The experiments performed here to probe the effect of water on the oxygen uptake showed clear evidence of the effect of water on the oxygen balance of the catalyst. First, the unsupported bulk PdO catalyst was reduced at 700 K with pure methane pulses injected at 6 min time intervals in a pure helium stream flowing continuously over the catalyst. The evolution of methane conversion with the pulse numbers depicted in Fig. 5 confirmed the higher activity of the partially reduced PdO catalyst reported earlier [8,15,16] and discussed in detail elsewhere [8]. Second, in the experiments where labeled oxygen pulses were injected into a pure or water-containing helium carrier flowing continuously over the partially reduced catalyst at 700 K, important differences were observed in the distribution of oxygen isotopomers in the reactor effluent between the “dry” and the “wet” carriers. The distributions of isotopomers with *m*/*z* values of 32, 34 and 36—standing for $^{16}O_2$, $^{16}O^{18}O$ and $^{18}O_2$, respectively, are given in Figs. 6–8. Our earlier work gave evidence that the isotopic exchange of oxygen between surface and the gas phase is impeded during methane oxidation over the oxidized Pd catalyst [6], in agreement with results reported by other groups [1,5,17]. We proposed this effect is due to water blocking oxygen exchange. The current experiment confirms this mechanism showing that oxygen exchange is seriously impeded in the presence of water.

The last interesting observation is apparent from the oxygen material balance performed at the end of the experiments following reduction of the catalyst after labeled oxygen pulses. The oxygen content of the

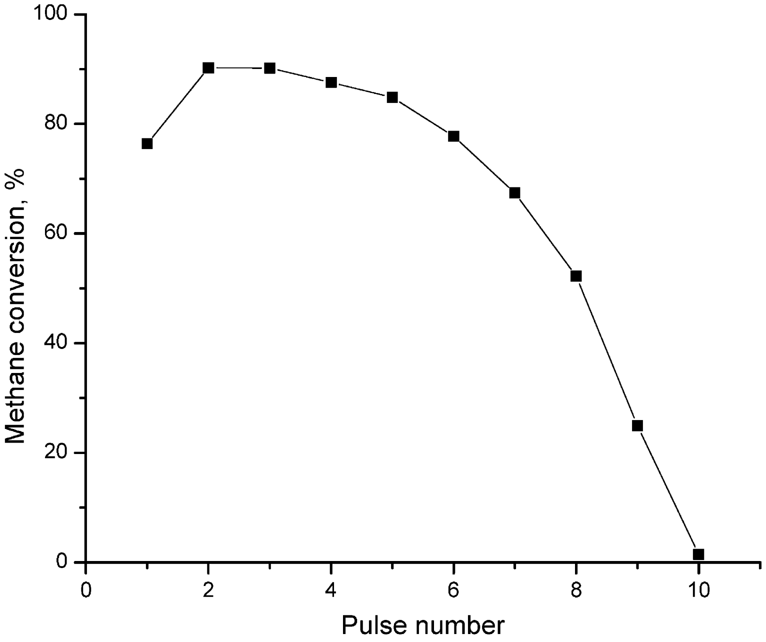

Fig. 5. Methane conversion observed during reduction of the catalyst with pure methane pulses.

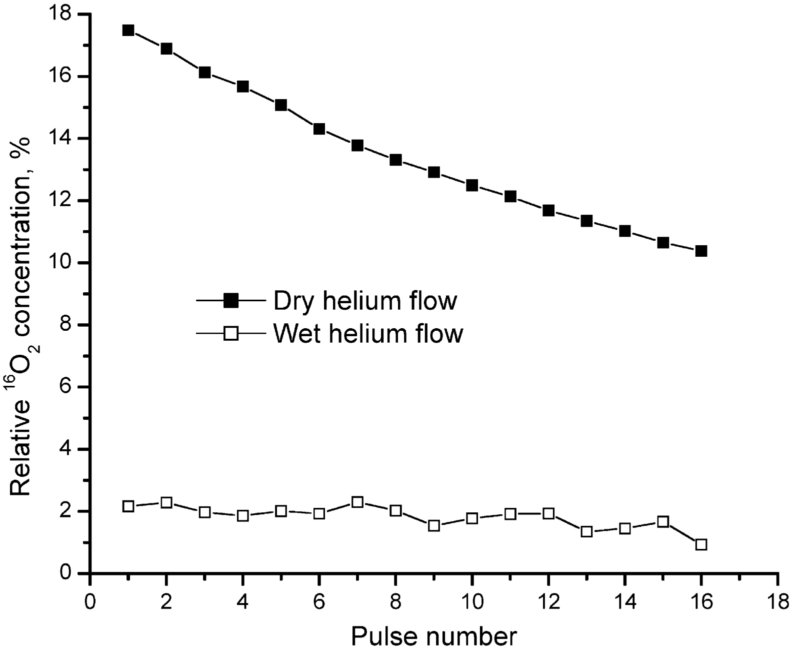

Fig. 6. Relative distribution of the oxygen isotopomer with $m/z = 32$ in the reactor effluent following labeled oxygen pulses injected in "dry" and "wet" carriers.

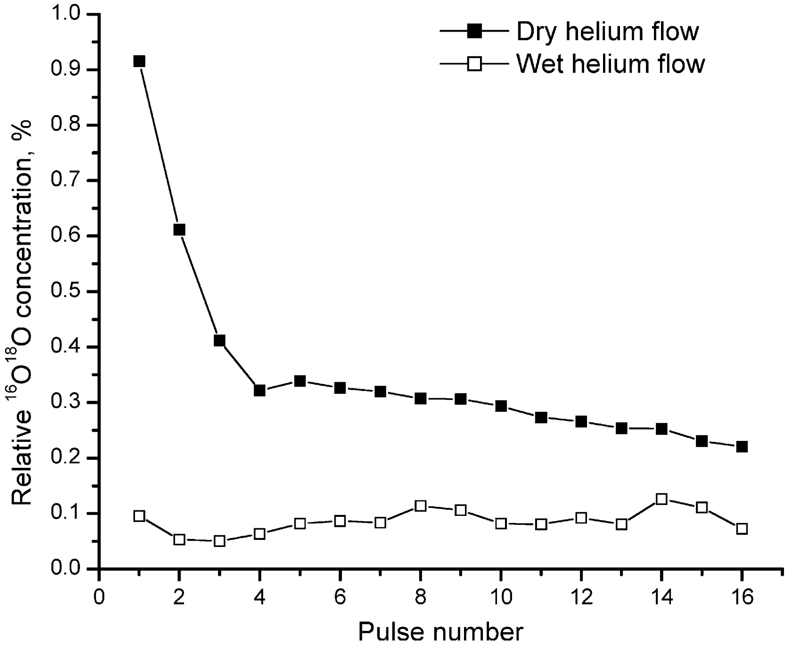

Fig. 7. Relative distribution of the oxygen isotopomer with $m/z = 34$ in the reactor effluent following labeled oxygen pulses injected in "dry" and "wet" carriers.

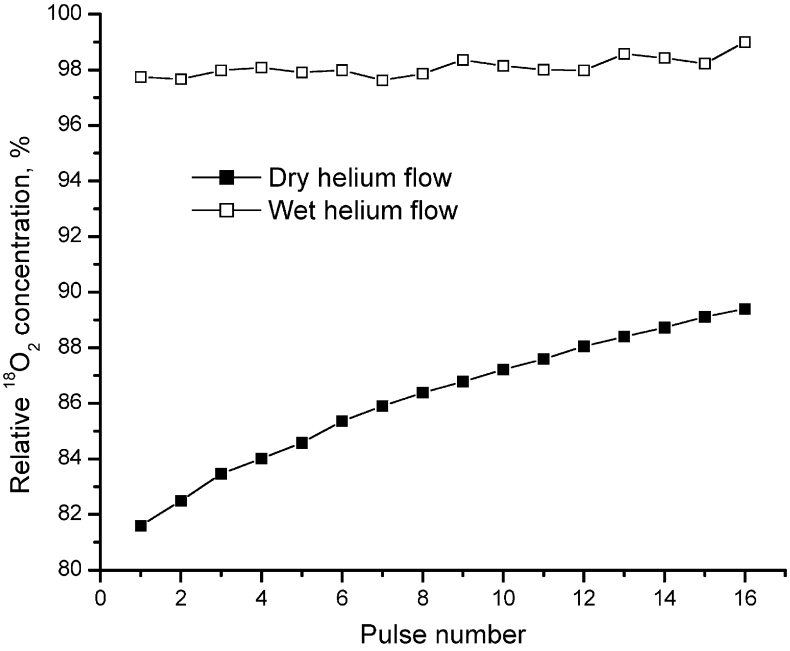

Fig. 8. Relative distribution of the oxygen isotopomer with $m/z = 36$ in the reactor effluent following labeled oxygen pulses injected in "dry" and "wet" carriers.

Table 1
Oxygen material balance during oxygen uptake measurements on slightly reduced, clean and water covered PdO surfaces

	Clean PdO	Water covered PdO
Oxygen content of the fully oxidized catalyst (g-at.)	2.50291E−05	2.49274E−05
Oxygen consumed during partial reduction (g-at.)	3.50053E−06	3.42035E−06
Oxygen content of partially reduced catalyst (g-at.)	2.15285E−05	2.15070E−05
Oxygen content of the pulsed reoxidized catalyst (g-at.)	2.48971E−05	2.14983E−05
From which:		
^{16}O	2.00335E−05	2.14459E−05
^{18}O	4.8635E−06	5.24E−08
Oxygen uptake during reoxidation with pulses of $^{18}O_2$ (g-at.)	3.3689E−06	−8.7E−09

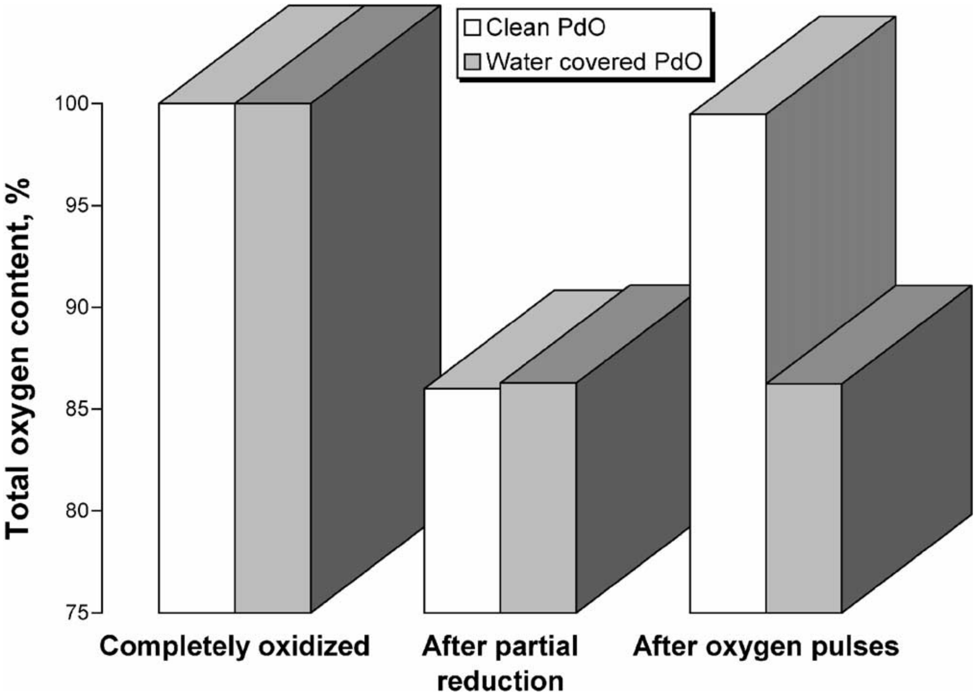

Fig. 9. The oxygen content of the catalyst at different stages of oxygen uptake experiment performed under "dry" and "wet" carrier experimental conditions.

catalyst at different stages of the experiment is given in absolute values in Table 1, and the percent of oxygen in the catalyst relative to the completely oxidized one after different pretreatments is depicted in Fig. 9. The data in Table 1 and the oxygen mass balance in Fig. 9 indicate that water inhibits both the oxygen exchange between the catalyst and the gas phase, and the oxygen uptake from the gas phase.

It should also be mentioned that no $H_2{}^{18}O$ has been detected in the reactor effluent during labeled oxygen pulses injected in the water-containing helium carrier, even though some ^{18}O was detected in the water and carbon dioxide produced during catalyst reduction after the labeled oxygen pulse series.

4. Discussion

Most mechanistic and kinetic studies of methane oxidation over Pd-based catalysts have been carried out under a continuous flow regime [3–5,9,18–20]. Different information is obtained using pulsed conditions. This is mainly because the pulse mode reduces the inhibition effect caused by the reaction products by completely eliminating them during the time interval between consecutive pulses, thus exposing a "clean" surface to each reaction mixture pulse. A low number of turnovers per site can be achieved by correlating the pulse volume and the amount of the catalyst in the reactor for each pulse. Reaction mechanism studies can, thus, follow the reactant–catalyst interaction in a step-wise manner.

The benefits of the pulsed technique described above are well reflected in the results reported in this study. By limiting the number of turnovers per site, the difference in the distribution of labeled oxygen atoms in water and carbon dioxide has been observed. We attributed this effect to the slower rate of water desorption as compared to CO_2 [6] and proposed that, because of the slow water desorption compared with the rate of equilibration between bulk and surface oxygen, the hydrogen samples the bulk and CO_2 is reflective of the instantaneous surface oxygen isotopic distribution. This explanation suggests that the mechanism of water inhibition effect may be related with the surface oxygen balance.

The starting point in probing this hypothesis is to understand the processes taking place under the reaction conditions used. The first labeled reaction mixture pulse contacts a fully oxidized and pure $Pd^{16}O$ surface. Methane is most likely dissociatively adsorbed on a PdO ion pair generating a surface hydroxyl and a methyl fragment bound to the palladium ion. The methyl fragments are further oxidized with surface oxygen generating hydroxyl groups and adsorbed CO_2. The carbon dioxide is rapidly desorbed and the vacancies at the surface are refilled with oxygen either from the bulk or from the gas phase. We showed that the $^{16}O/^{18}O$ ratio at the catalyst surface is determined by the ratio between the rates of the two reoxidation processes [6]. We also showed that the rates of the two concurrent processes respond differently to temperature changes. The lattice oxygen consumption, which indirectly reflects the rate of bulk oxygen diffusion, is strongly influenced at lower temperatures, while the uptake of gas phase oxygen is also consistent with the exponential evolution predicted by an activated process. However, the presence of water at the surface influences the relative rates of these processes in that it impedes oxygen uptake to the surface from the gas phase and, therefore, should be accounted for.

The experiments pulsing labeled oxygen presented here clearly showed the water covered surface has a considerably lower activity for isotopic scrambling of oxygen compared with the clean PdO surface. The catalyst was partially reduced initially and was almost completely reoxidized under "dry" conditions with 16 pulses of 500 μl of labeled oxygen in helium mixture; however, it was not reoxidized under "wet" conditions (see Table 1 and Fig. 9). This effect provides an explanation for why oxygen uptake is impeded by reaction where water is produced.

An interesting evolution is observed for mixed versus homogeneous oxygen isotopes resulting from the clean PdO surface (see Fig. 7). While the concentration of the homogeneous isotopes varies linearly with the pulse number—see the almost straight lines for the evolutions of $^{16}O_2$ and $^{18}O_2$, the concentration of the mixed isotope ($m/z = 34$) decreases sharply with the first three pulses and then stabilizes to a considerably lower rate. We assign this behavior to the catalytic effect for the oxygen isotopic exchange of the reduced palladium at the PdO surface. We have observed a similar increase in the rate of mixed isotope formation with a zirconia-supported palladium catalyst [21]. The higher rate levels off as the surface reduced states are reoxidized at higher pulse numbers. From these results we propose that the homogeneous isotope is formed by oxygen scrambling with the fully oxidized PdO surface and the mixed isotope is generated more effectively in the presence of surface reduced states. Oxygen dissociates at metallic palladium surfaces. The (1 1 0) and (0 0 1) PdO surfaces expose only a single type of oxygen species: an oxygen atom bridge bound to two Pd atoms. Both surfaces are polar and, thus, must reconstruct to maintain charge neutrality. Removing half the surface oxygen atoms from the bulk-terminated PdO (0 0 1) and (1 1 0) 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. Our experimental evidence is consistent with this theoretical interpretation showing that oxygen cannot dissociate on a fully oxidized PdO surface, as we discussed in the past work [6]. However, a simultaneous, double exchange mechanism would make it possible to form the homogeneous $^{16}O_2$ isotopomer when $^{18}O_2$ interacts with the ^{16}O oxide surface. This double exchange does not involve preliminary dissociation of oxygen at the surface as it can take place without formation of the mixed oxygen isotope, and it is likely responsible for the formation of $^{16}O_2$ observed in oxygen isotopic exchange of oxygen between the gas phase $^{18}O_2$ and the pure ^{16}O oxide surface reported elsewhere [21].

The explanation proposed here is also consistent with the distribution of labeled oxygen into the catalyst grain depicted in Fig. 10, observed during reduction experiments performed on the PdO catalyst after the experiment depicted with solid symbols in Figs. 6–8, where labeled oxygen pulses were injected in “dry” helium. It is clear that most of the labeled oxygen remains in the first surface layers. This is due both to the low rate of oxygen diffusion from the bulk and the decrease in the concentration of vacancies through reoxidation. In contrast with the different isotopic distribution of labeled oxygen in CO_2 and water produced during labeled reaction mixture pulsed experiments depicted in Fig. 4, the reaction products obtained from reduction with methane pulses showed the same isotopic distribution of oxygen. This suggests that the bulk oxygen diffusion is low relative to the rate of surface reduction with methane and metallic palladium is present at the surface.

It is also worth mentioning that, since no labeled water was observed during labeled oxygen pulses injected in the “wet” carrier, the rates of water adsorption and desorption are very slow, consistent with our proposal that water desorption is not equilibrated under many methane combustion experimental conditions [7]. The rate of hydroxyl recombination and water desorption from the surface has been observed to be much lower than that of carbon dioxide [7], so that the following two processes are likely: (i) before water is desorbed, the isotopic composition of the surface oxygen is equilibrated with the bulk; and (ii) the oxygen vacancies resulting from water desorption are refilled mostly with oxygen from the bulk because the oxygen introduced with the labeled pulse was flushed out from the reactor before the water is desorbed. The sequence of phases for the processes described above is represented schematically in Fig. 11.

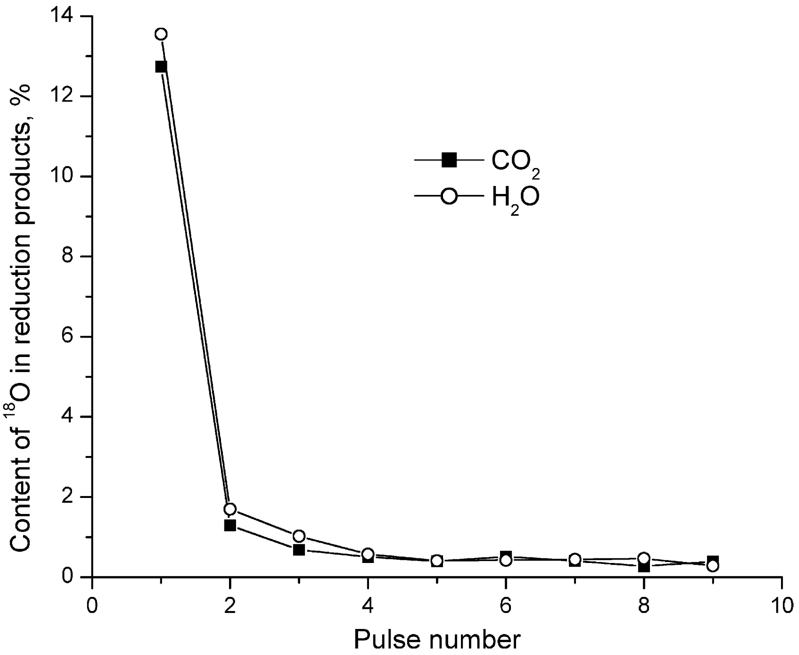

Fig. 10. Distribution of labeled oxygen in reaction products during PdO reduction after labeled oxygen pulses injected in “dry” helium carrier.

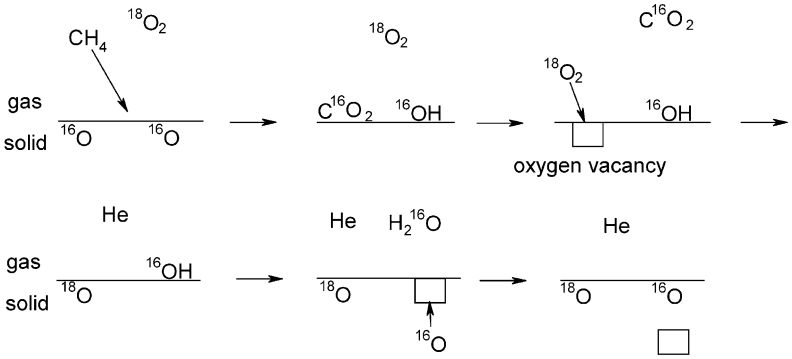

Fig. 11. Oxygen transfer processes that describe the behavior of the catalyst under labeled pulsed experimental conditions.

The results reported here are in agreement with the absence of the isotopic scrambling of oxygen between the catalyst surface and the gas phase in the presence of methane reported in the literature [5,6,17,22], and are consistent with the Pd–O ion pair site structure proposed for the dissociation of methane at the PdO surface [23,24]. At the PdO surface, oxygen from the gas phase can be dissociated on oxygen vacancy sites, as discussed in detail elsewhere [6]. If the vacancies are blocked by water, the surface is inactive for the isotopic exchange of oxygen. In the presence of methane, dissociation of the C–H bond and the subsequent oxidation of the methyl fragment generate more reduced sites at the surface capable of adsorbing oxygen from the gas phase. However, the oxygen uptake from the gas phase is limited by the recombination of surface hydroxyls and desorption of water molecules. Since many kinetic studies of methane combustion on PdO catalysts [4,15,18,25] reported zero reaction order with respect to oxygen, dissociation of methane on a surface site involving a surface oxygen vacancy is unlikely. However, surface vacancies need to be refilled in order to be able to participate in oxidation reactions, therefore water blocking surface reoxidation may be the mechanism responsible for the well-known water inhibition effect reported with PdO-based catalysts by many authors.

The differences in the rates of thermal decomposition of PdO under reaction conditions suggest that the support not only provides oxygen for the reaction at PdO surface, as demonstrated in the isotopically labeled pulsed experiment presented here, but may also play an important role in reoxidizing bulk oxygen vacancies in the PdO particles [21], thus impeding nucleation of reduced palladium, which is, most likely, the rate limiting step in the PdO thermal reduction process.

5. Conclusion

The results presented here reconfirmed the redox reaction mechanism for methane combustion on a PdO surface. Direct experimental evidence was also provided to show that water inhibits the exchange of oxygen between PdO and the gas phase. Dissociation of a methane molecule forms a hydroxyl group and a methyl fragment. Recombination of surface hydroxyls and water desorption is the rate limiting process for the regeneration of the active sites because it blocks the oxygen uptake from the gas phase. Therefore, it is proposed that the mechanism of water inhibition consists of the hydroxyls blocking the reoxidation of the catalyst. The slow rate of water desorption from the surface was also evidenced by the absence of labeled water isotopomer in the reactor effluent during labeled oxygen pulses injected in the water-containing helium carrier. The oxygen isotopic exchange experiments on partially reduced PdO gave direct evidence that oxygen is not dissociatively adsorbed on a completely oxidized PdO surface as consistent with charge balance arguments.

The stabilizing effect of the support for the PdO particles may be related to the oxygen transfer from the support to the PdO particles. The rapid and important oxygen transfer from the support to the PdO particle is evidenced in this study at temperatures as low as 700 K.

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