Oxygen Exchange between Palladium and Oxide Supports in Combustion Catalysts

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Temperature programmed isotopic exchange (TPIE) of oxygen and pulsed methane combustion experiments were used to investigate the contribution of oxygen from the support in the methane combustion reaction over alumina- and zirconia-supported palladium. TPIE experiments show that PdO is more active than reduced palladium for oxygen exchange between the catalyst and gas phase. Experiments performed on initially reduced catalysts produced a partially oxidized palladium phase containing both oxygen isotopes, suggesting that oxygen exchange between solid phases proceeds simultaneously with Pd oxidation. Reactivity tests performed with labeled reaction mixture pulses showed an important contribution of the support in the overall oxygen balance. Adsorbed oxygen is much more rapidly exchanged on zirconia-supported Pd than on alumina-supported Pd, and the isotopic exchange between the gas phase and the catalyst is strongly accelerated in the presence of methane. This is assigned to an increase in the concentration of oxygen vacancies in the support via oxidation of reaction intermediates on the support.

Introduction

Extensive research has been carried out to understand surface mobility of reactive species. It is well established that surface migration may represent an important step in catalytic cycles for the transfer of reaction intermediates between active sites during reactions, in catalyst activation, in the prevention of the catalyst deactivation, and in catalyst regeneration.

Hydrogen mobility has been the focus of many publications over the past decades. Spillover was defined as involving the "transport of an active species adsorbed or formed on a first phase onto another phase that does not under the same condition adsorb or form the species. The result may be the reaction of this species on the second phase with other adsorbed gases and/ or reaction with, and/or activation of the second phase".^{1,2} Hydrogen spillover was then presented as being involved in many reactions and used to tentatively explain many intriguing results.

Much less attention has been paid to oxygen mobility. Delmon was one of the first to outline the importance of spillover of oxygen in selective catalytic oxidation reactions,^{3–11} for induced phase stabilization, for preventing catalyst deactivation,¹² and for catalyst regeneration processes.¹³ Oxygen mobility was evidenced from the synergetic or cooperative effect observed between phases of multicomponent catalysts used in industrial oxidation processes.^{14,15} A new type of mechanism, denoted *remote control*, was used to explain the specific activity of a group of mechanical mixtures of metal oxides (MoO₃–Sb₂O₄, SnO₂–Sb₂O₄, ...) in the selective catalytic oxidation of isobutene to methacrolein.^{16,17} More recently, it has been proposed that oxygen spillover may induce the creation of new selective sites via surface reconstruction during the reaction.^{6,11,18}

In reviewing studies of direct oxygen mobility measurements, the isotopic exchange between ¹⁸O and ¹⁶O proved to be a powerful technique to study migration processes on oxides.^{19,20} This methodology was, for example, successfully applied to evidence surface oxygen mobility during selective oxidation on multicomponent oxide catalysts.²¹ On simple oxides, kinetic and mechanistic information was collected. More recently, studies of Duprez et al.²² concentrated on the investigation of oxygen activation on oxide-supported metal catalysts, which represents the first step of the migration process. In fact, the metal particles were considered to act as portholes for the subsequent migration of oxygen on the oxide support. Therefore, the role of the metal is believed to be crucial and the influence of various parameters has been analyzed.^{19,22} The presence of rhodium was observed to significantly accelerate oxygen exchange between the gas phase and the support: the maximum rate of exchange was observed at much lower temperatures (by 200-300 K) in the presence of Rh. This was attributed to the spillover of oxygen from the rhodium particles onto the support.²³

Our recent studies using isotopically labeled reaction mixture for the methane combustion reaction over pure and supported PdO particles²⁴ showed an important contribution of lattice oxygen from both bulk PdO and the zirconia support to the combustion reaction mechanism, suggesting an important oxygen exchange process between PdO bulk and surface and between the PdO phase and the support. It was also shown that isotopic scrambling between oxygen molecules in the gas phase and the catalyst surface does not take place in the presence of methane, while other authors²⁵ reported that it is important in the absence of methane.

In the present work we report on the oxygen exchange at high temperature between the metallic palladium phase and zirconia and alumina supports, investigated by isotopic exchange

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and measurements of the distribution of labeled oxygen among reaction products following pulses of reaction mixture labeled with $^{18}O_2$.

Experimental Section

Zirconia- and α -alumina-supported palladium catalysts denoted ZS and AS, respectively—were prepared by wet impregnation of the corresponding supports with palladium nitrate solutions to give approximately 3% (by weight) metallic palladium loading for the final catalysts. Subsequently, the catalysts were dried overnight at room temperature and then calcined in air at 550 °C for 6 h. The resulting catalysts were previously characterized²⁶ by X-ray diffraction before and after being cycled between room temperature and 900 °C in flowing reaction mixture. It has been shown²⁶ that the particle size distribution and combustion activity resulting after one heating cooling cycle as described above remain constant for further heating—cooling cycles; therefore, catalyst samples cycled once between room temperature and 900 °C in flowing reaction mixture will be further referred to as "stabilized".

The experimental setup has been described in detail elsewhere.²⁷ Pulsed isotopic exchange (PIE) experiments and combustion experiments with labeled oxygen in the reaction mixture were performed at atmospheric pressure, injecting pulses of 0.5 mL of either 4% $^{18}O_2$ in He or 4% $^{18}O_2$ and 1% CH₄ in He from Isotec, in a research grade 5.0 He carrier stream (Airgas, less than 1 ppm oxygen) flowing continuously over 35 mg of catalyst loaded into reactor.

Before PIE experiments, the empty reactor was tested in pulsed mode for catalytic activity in oxygen exchange. There was no oxygen exchange activity observed at temperatures below 740 °C. Above this temperature, detectable amounts of mixed oxygen isotope (i.e., ¹⁶O¹⁸O) were observed in the reactor effluent. Also, both supports were tested for activity in the methane combustion reaction. Neither of them showed detectable methane conversion, suggesting they are not able to activate methane under the experimental conditions used in this study.

The isotopic distribution of oxygen into the catalyst at different stages of experiments was determined by reduction of the catalyst with pulses of 5% hydrogen in He (Airgas) at 130 °C. The reduction was considered completed when only hydrogen was detected in the reaction effluent. It is assumed that, at this temperature and time scale of our experiments (pulses injected at a constant time interval of 80 s), there is no significant oxygen exchange between the PdO phase and the support, as evidenced in past work.²⁴ Although the distribution of labeled oxygen may be altered by isotopic scrambling of oxygen with the catalyst via water molecules produced during catalyst reduction with diluted hydrogen, the short contact time used and the use of diluted hydrogen significantly limit readsorption of water produced. This was demonstrated recently in an experiment showing no oxygen exchange for the water molecules with the catalyst surface.²⁸ Also, the inhibitory effect of water, known to alter the combustion activity of oxidized palladium catalyst, was shown to have no effect on the metallic state of the catalyst.²⁶ Therefore, although we cannot completely rule out the possibility of isotopic oxygen scrambling via water molecules, under our experimental conditions such a process is likely to have little influence, if any, on the final results of reduction experiments.

ESR spectra for zirconia samples following evacuation for 6 h at room temperature and at 300 °C, and after admission of 15 Torr of oxygen at room temperature after evacuation for 6 h at



Figure 1. TPIE profiles for reduced (solid symbols) and oxidized (open symbols) palladium catalysts supported on zirconia (circles) and alumina (triangles).

300 °C were recorded at room temperature using a Bruker ESP 300E spectrometer.

Results

Isotopic Exchange of Oxygen at Low Temperatures (100– 500 °C). Temperature programmed isotopic exchange (TPIE) profiles were determined for both zirconia and aluminasupported catalysts, initially in either reduced or oxidized states. Stabilized samples weighing 35 mg were heated at 5 °C/min between 100 and 500 °C in flowing helium. At 150 °C pulses of 0.5 mL of 4% ¹⁸O₂ in helium were injected in the carrier stream at constant time intervals of 80 s continuously monitoring the distribution of oxygen isotopomers in the reactor effluent. Similar experiments were performed with stabilized samples previously reduced with hydrogen at 50 °C for 30 min, then heated in helium flow to 350 °C to decompose any palladium hydride formed during reduction, and cooled to 100 °C to start the temperature program. Each experiment was performed on fresh, stabilized catalysts samples.

The onset of the isotopic exchange was evidenced by the formation of the mixed isotopomer ¹⁶O¹⁸O. The evolution of the concentration of ¹⁶O¹⁸O isotopomer during TPIE experiments over reduced (solid symbols) and oxidized (open symbols) catalysts is shown in Figure 1.

The oxidized catalysts have quasi-superimposable TPIE profiles suggesting that, for oxidized catalysts at low temperatures, the isotopic exchange is not affected by the support. However, reduced catalysts behave quite differently. Isotopic exchange is observed at higher temperature for both zirconiaand alumina-supported particles compared to the oxidized catalysts, with ZS exchanging at slightly lower temperature. Also, the rate of oxygen exchange for the catalyst supported on alumina is lower than that for zirconia-supported particles at the same temperature.

The distribution of the homogeneous isotopes ($^{16}O_2$ and $^{18}O_2$; not shown) resulting during TPIE with the oxidized catalysts showed no significant changes as temperature was increased. However, the zirconia-supported reduced catalyst showed higher oxygen exchange activity with respect to the double isotopic exchange (i.e., production of $^{16}O_2$), but the isotopic distribution changed with the temperature only for the first four labeled oxygen pulses in the low-temperature region (<175 °C), after which no significant change could be observed as the temper48.3

31.8

pulse no.

ZS

AS

TABLE 1: Distribution of Water Isotopomers following Hydrogen Pulses after TPIE with Reduced Catalysts

47.6

63.3

ribution of water isotopomers following Hydrogen Pulses after TPTE with Reduced Catalysis										
1	1	2	2	3	3	4	4	5	5	
H ₂ ¹⁶ O	H218O	H2 ¹⁶ O	H2 ¹⁸ O	H2 ¹⁶ O	H ₂ ¹⁸ O	H2 ¹⁶ O	$H_2^{18}O$	$H_2^{16}O$	H ₂ ¹⁸ O	

56.6

43.2

ature increased. The higher, but constant concentration of ${}^{16}O_2$ for the reduced zirconia-supported catalyst suggests that the double oxygen exchange is produced at the surface of the slightly reduced zirconia support.

51.7

68.2

52.4

36.7

To measure the oxygen uptake by the initially reduced catalysts during TPIE experiments, pulses of 0.5 mL of diluted hydrogen (5% in helium) were injected at 130 °C over the catalysts after the last labeled oxygen pulse of each TPIE experiment performed on an initially reduced catalyst sample. At the same temperature, both initially oxidized catalysts required nine pulses of diluted hydrogen until no water was detected in the reactor effluent, suggesting only oxygen from the PdO phase is used for hydrogen oxidation. The distribution of oxygen isotopomers in the water resulting following hydrogen pulses is given in Table 1.

The initially reduced catalysts are partially oxidized during the TPIE experiment, as predicted by the phase diagram of palladium at the temperature and oxygen partial pressure of our experiment. The newly oxidized catalysts contained both ¹⁶O and ¹⁸O. The reduction results clearly indicate that the zirconiasupported catalyst has a higher oxidation rate than AS, thus consuming more hydrogen for reduction. Another interesting observation is that the total fraction of labeled oxygen in the catalysts after TPIE experiments is higher (0.628) for the AS catalyst than for ZS (0.415). This suggests that more oxygen from the support is used to reoxidize the metallic particles in the case of ZS than in the case of AS. Another potential explanation would be that the rate of oxygen exchange between the newly oxidized Pd18O and the support containing only 16O is higher for zirconia than for alumina. However, both hypotheses suggest a major role of the oxygen from the support. Assuming a layer-by-layer reduction mechanism for hydrogen pulses, the reduction results also indicate a higher concentration of the labeled oxygen at the surface of alumina-supported catalyst, consistent with the lower rates for reduction and oxygen exchange with the support.

Palladium oxide is more active than metallic palladium for oxygen exchange with the gas phase. The reduced catalysts exchanged oxygen at higher temperatures than the oxidized ones. Moreover, the oxidized catalyst supported on alumina behaved similarly to that supported on zirconia confirming that, over the temperature range studied, the support has no influence on the isotopic exchange of oxygen between PdO and the gas phase likely because exchange between the gas phase and PdO is much faster than exchange between PdO and the support or between the support and the gas phase.

Isotopic Exchange of Oxygen at High Temperature (680 °C). Isotopic exchange experiments were performed at 680 °C with equal amounts of reduced catalysts and, separately, with the supports. Pulses of 4% $^{18}O_2$ were injected in a helium carrier flowing continuously over the samples. The results are depicted in Figures 2 and 3.

Bare zirconia and zirconia-supported palladium particles behaved similarly, suggesting the presence of metallic particles at the zirconia surface has little, if any, influence on the rate of oxygen exchange with the gas phase. However, metallic palladium is known to dissociatively chemisorb oxygen, thus to promote formation of the mixed isotopomer, consistent with higher concentrations of the mixed isotopomer observed in our



Figure 2. Distribution of oxygen isotopomers following pulses of labeled oxygen ($^{18}O_2$:He) over zirconia-supported palladium (solid symbols) and bare zirconia (open symbols) at 680 °C.



Figure 3. Distribution of oxygen isotopomers following pulses of labeled oxygen (${}^{18}O_2$:He) over alumina-supported palladium (solid symbols) and bare alumina (open symbols) at 680 °C.

experiments for the ZS case. This is clear evidence that dissociated oxygen at the metallic surface can migrate onto the support to recombine with oxygen atoms from the support and desorb as mixed isotope, and that this process is catalyzed by the metallic particle.

By contrast, the alumina support and the catalysts supported on alumina behaved quite differently. On one hand, neither the alumina-supported catalyst nor the bare alumina support produces measurable ¹⁶O₂ under our isotopic exchange conditions. On the other hand, even though both supports have comparable specific surface areas (150 and 120 m² g⁻¹ for alumina and zirconia, respectively), the alumina-based samples exchanged less oxygen than the zirconia systems, consistent with results reported by Duprez.¹⁹

Isotopic Exchange of Oxygen during Methane Combustion at High Temperature (680 °C). Combustion activity Oxygen Exchange between Pd and Oxide Supports



Figure 4. Distribution of O_2 isotopomers after labeled reaction mixture pulses (${}^{18}O_2$:CH₄:He) injected over reduced catalysts at 680 °C.

measurements were performed with labeled reaction mixture pulses injected at 680 °C over the reduced catalysts. At this temperature and oxygen partial pressure the Pd catalyst is not converted to PdO during reaction. The conversions recorded with each catalyst did not change from pulse to pulse, and—as expected for similar metal loadings, particle size, and reaction conditions—did not change significantly for catalysts dispersed on different supports ($35.5 \pm 0.5\%$ for AS and $34.2 \pm 0.5\%$ for ZS), suggesting no influence of these supports on the catalytic activity. Constant conversion pulse to pulse is also a strong indication that there is no change in the palladium oxidation state.

In the presence of methane the alumina-supported metallic Pd catalyst exchanged considerably more oxygen compared to oxygen-only pulses, as depicted in Figure 4. The oxygen exchange with the gas phase increased also for the zirconiasupported catalysts, but to a lesser extent. It should be mentioned that in our previous work with labeled reaction mixture pulses over an oxidized palladium catalyst²⁴ the oxygen exchange between the gas phase and the surface is limited by reaction, in agreement with results reported by other authors.²⁵ This same effect of reaction-generated vacancies is likely the route by which oxygen exchange between the palladium phase and the support, and thus oxygen exchange with the gas phase, is accelerated in the presence of methane. This effect is not pronounced in the case of zirconia where equilibration with the bulk is fast and the stationary state concentration of surface vacancies is not significantly perturbed.

The distribution of ¹⁸O in the reaction products following reaction mixture pulses labeled with ¹⁸O₂ over the catalysts containing only ¹⁶O is shown in Figures 5 and 6 for CO₂ and water, respectively. While there are notable differences between the distributions of oxygen in the carbon dioxide resulting from both catalysts, the concentrations of ¹⁸O atoms in the water produced in the methane combustion reaction over alumina- and zirconia-supported catalysts are very close. This major difference is clearly illustrated in Figure 7 where distributions of the ¹⁸O atoms in reaction products are plotted against the pulse number for the catalysts studied. Differences in ¹⁸O distribution for the two catalysts are remarkable with respect to the oxygen and carbon dioxide evolving from the reactor, water showing the same distribution of the labeled oxygen isotope for both



Figure 5. Distribution of CO_2 isotopomers after labeled reaction mixture pulses (${}^{18}O_2$:CH₄:He) injected over reduced zirconia-supported catalysts (solid symbols) and alumina-supported catalysts (open symbols) at 680 °C.



Figure 6. Distribution of water isotopomers after labeled reaction mixture pulses ($^{18}O_2$:CH₄:He) injected over reduced zirconia-supported catalysts (solid symbols) and alumina-supported catalysts (open symbols) at 680 °C.

catalysts. It should also be noted that, for both products (oxygen and CO_2), the concentration of ¹⁸O is higher for the combustion reaction over alumina-supported catalyst, suggesting a lower contribution of oxygen from this support to the reaction mechanism compared to zirconia. This is consistent with zirconia having higher oxygen mobility than alumina.

Methane combustion experiments were also performed without oxygen in the gas phase by injecting pulses of 1% methane in He over the reduced catalysts at 680 °C. Under these experimental conditions, the support is the sole source of oxygen. It should be kept in mind that none of the supports showed methane activation with reaction mixture at this temperature. Following diluted methane pulses, both carbon oxides were detected as reaction products and used to compute the overall methane conversion and oxygen consumption from the support. The values determined for the two catalysts are depicted against the pulse number in region (b) of Figure 8. In region (a) of the same diagram, conversions of the reaction mixture pulses (in the presence of gas-phase oxygen) are given for comparison.



Figure 7. Concentration of the ¹⁸O atoms in reactor effluent following labeled reaction mixture pulses (${}^{18}O_2$:CH₄:He) injected at 680 °C over palladium particles supported on alumina (open symbols) and zirconia (solid symbols).



Figure 8. Methane conversions observed following pulses of reaction mixture (region (a)) or 1% methane in helium (region (b)) injected at 680 °C over supported palladium catalysts.

The conversion observed with the first pulse of diluted methane is higher than those observed with reaction mixture, consistent with the -1 reaction order with respect to oxygen reported for metallic palladium catalysts.²⁹ Methane conversion decreased for both catalysts as the number of pulses increased. However, the activity of the alumina-supported catalysts decreased steeply, while the zirconia catalyst lost its oxidation activity at a relatively slow rate, preserving much of its initial activity even after 90 pulses of diluted methane. The change in methane conversion as the oxygen from the support is depleted was determined from the oxygen material balance and is depicted in Figure 9. At the steady state level-off point the reaction rate is limited by oxygen diffusion in the bulk of the support, which is considerably higher for zirconia compared to alumina.

The anaerobic methane oxidation experiments performed with the two catalysts (Figures 8 and 9) showed that the activity of the Pd/alumina catalyst decreases rapidly, which may be ascribed to the lower oxygen mobility in alumina. By contrast, oxygen vacancies created at the zirconia surface are rapidly refilled with bulk oxygen. This was evidenced by ESR experiments on





Figure 9. Evolution of methane combustion activity as a function of oxygen content of the support for palladium catalysts.



Figure 10. EPR spectra recorded at room temperature for a zirconia sample after evacuation for 6 h at room temperature (1) and 300 °C (2), and after admission of 15 Torr of oxygen over the sample annealed at 300 °C (3).

zirconia annealed at 300 °C; the ESR spectra were recorded at room temperature on (i) a sample outgassed for 6 h at room temperature, (ii) a sample outgassed for 6 h at 300 °C, and (iii) a sample contacted with 15 Torr of oxygen after outgassing at 300 °C. The spectra are given in Figure 10.

After evacuation at room temperature, the EPR spectrum (trace 1) shows a signal ($g_{\parallel} = 1.958$, $g_{\perp} = 1.976$) whose intensity strongly increases after heating at 300 °C (trace 2). This signal can be assigned to a 4d electron of Zr³⁺ ion, in agreement with values previously reported on ZrO₂.^{30–34} The spectrum recorded after admission of oxygen (trace 3) shows a decrease in intensity of the above signal and the appearance of a new one with $g_x = 2.004$, $g_y = 2.010$, and $g_z = 2.031$, characteristic for the O₂⁻ superoxide species on the ZrO₂ surface.^{35–37} The g_{\parallel} component of the Zr³⁺ ion, weaker but still present, is due to the contribution

of bulk Zr^{3+} ions, which are not accessible to gas-phase oxygen at room temperature. After evacuation of O₂ at room temperature, the EPR spectrum (not represented) is identical to the trace 2, evidencing the low stability of the superoxide species.

The genesis of oxygen vacancies, Zr^{3+} species and superoxide entities may be described as follows:³⁰

$$O_0^{x} \rightleftharpoons (1/2)O_{2(g)} + V_0$$

$$2Zr^{4+} + V_0 \rightarrow 2Zr^{3+} + V_0^{2+}$$

$$Zr^{3+} + O_{2(g)} \rightleftharpoons Zr^{4+} + O_2^{-}$$

with $O_0^x = O^{2-}$ ions in regular lattice position, and V_0 and $V_0^{2+} =$ oxygen vacancies with two and zero trapped electrons, respectively, according to Kröger notation.^{38,39}

Discussion

Role of the Noble Metal in the Oxygen Exchange at Low Temperatures. The chemisorption of oxygen on Pd may or may not lead to the formation of metal oxide, depending on the temperature and oxygen partial pressure. Our TPIE experiments showed that the support has no effect on the oxygen exchange activity of the oxidized catalysts, whereas it clearly influences the oxygen exchange activity of supported metal particles. The oxygen material balance determined from pulsed reduction of the catalyst after TPIE experiments performed on initially reduced catalysts demonstrated that the Pd-zirconia catalyst was more oxidized than Pd-alumina; this indicates a higher rate of palladium oxidation on the support with the highest oxygen mobility. Note that the reduction results given in Table 1 indicate that neither initially reduced catalyst was completely oxidized after the TPIE experiments. Independent of the support, both fully oxidized catalysts required nine diluted hydrogen pulses until no water formation was detected in the reactor effluent. In our previous temperature programmed reaction experiments,²⁶ supports with higher oxygen mobility (e.g., zirconia) showed a higher rate of activity recovery, associated with palladium reoxidation. The TPIE results presented here indicate that the zirconia support influences Pd oxidation at temperatures as low as 350-400 °C.

Under similar experimental conditions Duprez¹⁹ reported a lower rate of oxygen exchange for alumina than for zirconia. On the other hand, the oxygen from a surface monolayer of the PdO formed during methane combustion over a Pd foil was completely exchanged in 12 s at 325 °C and 5 Torr of oxygen partial pressure,⁴⁰ suggesting a relatively high oxygen exchange activity for PdO. The fully oxidized catalysts showed no differences in their TPIE profiles, although the reduced ones behaved quite differently. This is because the oxygen exchange activity of PdO particles is considerably higher than that of alumina or zirconia; thus the contribution of either support to the overall oxygen exchange activity of the fully oxidized catalysts is negligible.

The noble metal does not need to be completely oxidized in order to be active in oxygen isotopic exchange. This is consistent with the observation of Duprez²⁰ that prior reduction of the catalyst has little effect on the exchange, particularly for Rh catalysts. Therefore, the oxidation process and the oxygen exchange between the support and the noble metal phase are simultaneous processes. The different concentrations of labeled oxygen measured in the initially reduced catalyst after TPIE experiments (Table 1) could arise either from different rates of oxygen exchange between newly formed PdO and the supports



Figure 11. Oxygen exchange processes determining the isotopic composition of the palladium oxide phase resulting after TPIE experiments with initially reduced catalysts. (1) Oxygen uptake from the gas phase by the metallic particle, possibly catalyzed by the newly formed PdO phase at the metal—support interface. (2) Oxygen exchange between the newly formed PdO_x phase and the support. (3) Oxygen exchange between the PdO_x phase and the gas phase. (4) Oxygen exchange between gas-phase oxygen and surface oxygen from the support. (5) Equilibration of oxygen and surface oxygen vacancies with the bulk.

or from the involvement of support oxygen atoms in the Pd oxidation reaction, for example, at the metal-support interface. There is support for this interpretation from practical methane oxidation reactions as the reoxidation hysteresis can be almost eliminated for a well-dispersed palladium catalyst on a high oxygen mobility support. In previous work with isotopically labeled oxygen in the reaction mixture,²⁴ we observed that the rate of oxygen exchange between the PdO particles and the zirconia support is low at 323 °C, and it is expected to be even lower for particles supported on alumina because of the lower oxygen mobility in this support.

Based on these considerations, the influence of the support on the oxygen exchange activity at low temperatures is rather indirect. A possible mechanism would consist of the transfer of lattice oxygen from the support to the metal at the metalsupport interface. The freshly formed PdO promotes reoxidation of bulk Pd particle from the gas phase and also exchanges oxygen with the gas phase. Thus, the final isotopic composition of the fully oxidized palladium particles depends on the relative rates of the following processes: the oxygen uptake from the support and from the gas phase, the oxygen exchange with the gas phase, and equilibration between bulk and surface. These processes are represented by Figure 11. This is consistent with our observation of a high mobility support narrowing the activity hysteresis, and the high proportion of unlabeled oxygen found on re-reducing the palladium phase after oxidation during TPIE experiments with initially reduced catalysts (Table 1).

It should also be mentioned that the results reported here confirm that palladium is a poor promoter for oxygen exchange, in agreement with results reported by Duprez and co-workers from studies on palladium, platinum, and rhodium.^{22,23} However, the apparent contradiction between its poor performance in oxygen exchange and its good performance in methane combustion is consistent with the zero-order kinetics with respect to oxygen for methane combustion over palladium catalysts at low temperatures, which suggests the rate-limiting process does not involve oxygen exchange between the catalyst and the gas phase.

Role of the Noble Metal in the Oxygen Exchange at High Temperatures. Compared to alumina, zirconia has a much higher activity for oxygen dissociation at high temperatures. For this reason, the oxygen exchange activity is only insignificantly improved in the presence of palladium particles at the surface. Bare alumina is much less active for oxygen dissociation. However, because metallic palladium dissociates oxygen, the rate of oxygen exchange is considerably higher for alumina in the presence of Pd particles. It is noteworthy that aluminacontaining systems do not form measurable ¹⁶O₂ during isotopic exchange experiments (¹⁸O spills onto the support and exchanges with surface ¹⁶O, or ¹⁶O from the support oxidizes the Pd particles at the interface and is exchanged with ¹⁸O-adsorbed Pd⁰ adatoms). Moreover, at high pulse numbers, the distributions of oxygen isotopomers in PIE experiments performed with the AS catalyst and on bare alumina are close. This is most likely because equilibration between surface and bulk oxygen on alumina is very slow compared to that on zirconia. Once the oxygen at the surface is largely exchanged, further exchange is limited by the bulk transport.

The higher oxygen exchange activity of zirconia can be explained by its capability to form oxygen vacancies. The ESR experiments showed that oxygen-deficient centers at the zirconia surface are present after evacuation at room temperature and that bulk vacancies are formed via migration of bulk oxygen toward the surface at an evacuation temperature as low as 300 °C. Moreover, gas-phase oxygen reacts with surface defect centers to give O₂⁻ species; therefore, the presence of surface oxygen vacancies is the driving force for equilibration between bulk and surface and for oxygen exchange with the gas phase. The rate at which equilibration is approached on zirconia is expected to increase as the temperature increases, similarly to the rate of oxygen exchange with the gas phase as determined by Duprez et al.¹⁹ Because alumina has a more pronounced ionic character, it is much less susceptible to form oxygen vacancies, consistent with its low oxygen exchange activity and anaerobic methane oxidation activity (see Figures 3 and 9). However, as the alumina-supported catalyst is exposed to pulses of reaction mixture, the activity for oxygen exchange increases. This could be explained by the formation of oxygen vacancies at the catalyst surface, which would accelerate both the exchange with the gas phase and equilibration with the bulk; therefore, formation of ¹⁶O₂ becomes more probable at the initial stage of the experiment. This explanation is consistent with the results from the anaerobic oxidation of methane in that the activity dropped rapidly but stabilized at a small value greater than zero ($\sim 2\%$), suggesting a fairly constant flux of oxygen reaching the surface between consecutive pulses. By contrast, zirconia is depleted of a much higher amount of oxygen (nearly 15% of its total oxygen content) and the rate of equilibration between bulk and surface is high. The anaerobic methane oxidation activity drops very slowly with the reduction of support, indicating that most of the vacancies formed with one pulse of methane are refilled with oxygen from bulk during the time interval between consecutive pulses.

Role of Gas Phase and Support Oxygen in Methane Combustion at High Temperatures. As discussed above, because of the high activity for oxygen exchange of the zirconia support, the contribution of palladium in the oxygen exchange is negligible. However, palladium has a determinant role in the methane oxidation reaction, since bare zirconia showed no methane activation and methane activity is equivalent for both the AS and ZS catalysts and did not change with pulse number. The presence of metals at the surface of oxides was shown to promote the reduction of supports in the presence of hydrogen or other reducing species. For example, we³⁰ observed that, in the presence of palladium, the reduction temperature of zirconia by hydrogen is 200 °C lower compared with that for bare zirconia. However, the amount of oxygen available for surface oxidation reactions is determined by the oxygen mobility in the oxide supports, which is the ability of the material to rapidly equilibrate the oxygen vacancies between surface and bulk. In discussing the experimental results obtained from pulsed experiments with catalysts supported on alumina and zirconia, it is

useful to consider the reaction mechanism. The surface-assisted hydrogen abstraction from the methane molecule has been proposed as the initial step in the reaction mechanism over a wide range of reaction conditions.^{41–43} The result of methane activation is the formation of adsorbed hydrogen and methyl radicals. The overall reaction has been proposed to follow the Langmuir-Hinshelwood mechanism, through the interaction between adsorbed oxygen, carbon, and hydrogen species at the metallic Pd surface.²⁹ Thus, methane and oxygen competitively adsorb on the active site with the methane oxidation negative first order in oxygen, consistent with our anaerobic methane oxidation experiments showing higher methane conversions for the first diluted methane pulse injected after reaction mixture pulses with catalysts supported on both alumina and zirconia. The role of the support in the methane combustion mechanism over dispersed metallic palladium particles has not been previously addressed.

Although this mechanism is consistent with many kinetic studies, it cannot explain the high concentration of ¹⁶Ocontaining reaction products observed with the first labeled reaction mixture pulses in our experiments. The experimental results presented here suggest that the support contributes oxygen to the combustion reaction. There are differences in the distribution of labeled oxygen atoms among reaction products in labeled pulsed experiments for catalysts supported on the two carriers, despite their similar specific activities. At first, this could be assigned to differences in the isotopic scrambling reactions between surface and gas-phase molecules for the two supports. If this would have been the case, however, the lower exchange activity of alumina should have equally influenced the isotopic scrambling of water and CO₂ molecules. In fact, this is not observed since the isotopic distribution of water molecules observed with the alumina-supported catalysts follows approximately the same path observed for the zirconia-supported catalyst (see open squares and circles in Figure 7). Moreover, an experiment was performed with labeled reaction mixture pulses injected over a mechanical mixture of alumina and palladium powder (not shown). In this experiment the loading of alumina to Pd was approximately 4 times that of the supported catalyst. This level of alumina was used both to ensure methane conversion values close to those obtained with the supported catalysts and to avoid formation of hot spots. Here both water and carbon dioxide had the same distribution of the ¹⁸O isotope (as in the case of zirconia-supported catalyst). The equivalent distribution of oxygen in the products combined with the high ¹⁶O content in products resulting with the supported catalyst despite the lower alumina surface area exposed clearly indicates that the *difference* in 18 O distribution between water and CO₂ obtained with the alumina-supported catalyst is not caused by the isotopic scrambling of the desorbed reaction products with the alumina support. For the mechanical mixture, because there is little intimate contact between the metallic particles and the alumina in the reactor, both CO₂ and water products contained a higher concentration of labeled isotopomers compared with both supported catalysts.

Hence, we propose that methane molecules are activated on the metallic surface in competition with oxygen molecules from the gas phase. However, the isotopic distribution of the reaction products at small numbers of pulses indicates that oxygen from the support is used more effectively for methane oxidation than oxygen adsorbed from the gas phase. This could be an effect of the high binding energy for the dissociated oxygen at the metallic surface, as proposed by McCarty.⁴⁴ Consumption of the oxygen at the metal–support interphase may be kinetically

favored for methane oxidation. This consumption generates oxygen vacancies. The oxygen vacancies are refilled either from the gas phase or from the bulk of the support, the isotopic distribution of oxygen in the immediate vicinity of the metallic particle being determined by the relative rates of the two vacancy refilling processes. Because of the high oxygen mobility in zirconia, vacancies created near the metallic particles are rapidly refilled by migration of oxygen from the bulk and the gas phase, and the oxygen distribution at the surface is equilibrated. By contrast, the oxygen vacancies on the alumina-supported catalyst whose oxygen mobility is lower are refilled from the gas phase so that the concentration of ¹⁸O in products increases more rapidly, as seen for CO₂. The lower ¹⁶O concentration in water is most likely due to the higher mobility of surface hydroxyls as compared with carbonyl or carboxyl species. This higher mobility of surface hydroxyl makes it possible that the hydrogen is actually oxidized at the support surface, far from the metallic particle, where ¹⁶O is exchanged at a much slower rate.

In terms of reaction kinetics, based on the results observed here one would expect different reaction rates for palladium particles supported on carriers with different oxygen mobilities. This is not the case simply because the rate-limiting step is the dissociative methane adsorption on the metallic particle, which competes with oxygen adsorption. This is consistent with the negative first order kinetics with respect to oxygen reported by many studies. However, oxygen at the support/metal interface is likely kinetically favored for oxidation of the methane decomposition products. This is consistent with earlier observations that support identity and contact with palladium can influence the oxidation of palladium.

The anaerobic methane oxidation experiments showed a sustained oxidation activity of the zirconia-supported catalyst in which the only oxygen available for reaction came from the support, and the oxidation activity was high even after consumption of more than 10% of the oxygen contained in the support. This observation suggests that, although there is more than one source of oxygen for the fuel lean oxidation conditions, the reaction kinetics does not appear to be influenced by the relative rates of oxygen consumption from different sources. Both catalysts showed the same oxidation activity under the reaction mixture, whereas the oxygen used for the reaction came from different sources, thus suggesting that the activation of methane on Pd is the rate-limiting step.

The oxygen mobility in the support is of crucial importance for catalysts operating under fluctuating composition of fuel mixtures. As the reaction mixture becomes fuel rich, the reaction order with respect to oxygen becomes positive. Supports with low oxygen mobility, such as alumina, are susceptible to rapid deactivation, whereas those with high oxygen mobility can preserve a high activity for a significantly longer period of time, showing a potential to avoid oscillations or activity excursions associated with changes in the fuel composition. However, the rate of oxygen diffusion through the bulk determines the level of conversion maintained, as well as the time it is preserved under fuel-rich conditions.

Conclusion

The results presented here suggest that oxygen exchange is significant between the support and the noble metal phase during palladium oxidation at low temperatures, which precludes the production of Pd¹⁸O particles supported on carriers containing only ¹⁶O. The concentration of labeled oxygen in the completely oxidized palladium phase is determined by the oxygen mobility in the support.

The oxygen from the support also participates in the methane combustion reaction mechanism over supported metal particles. It is proposed that the oxidation of methane involves both oxygen adsorbed on palladium metal and surface oxygen from the support. However, while adsorption of oxygen from the gas phase competes with methane adsorption resulting in negative first order kinetics with respect to oxygen, reaction intermediates resulting from the activation of methane on the metal surface are preferentially oxidized at the interface or spilled over the support and oxidized by surface oxygen from the support, generating oxygen vacancies. For supports with high oxygen mobility, the vacancies are partially refilled with bulk oxygen, which leads to ¹⁶O-rich reaction products. By contrast, the oxygen vacancies created on the alumina surface are refilled mainly from the gas phase, which generates ¹⁸O-rich reaction products.

The oxygen mobility of the carriers appears of crucial importance for real applications with fluctuating fuel compositions; high mobility allows maintaining of reasonable oxidation activities under fuel-rich conditions.

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