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# Combustion of methane over palladium/zirconia: effect of Pd-particle size and role of lattice oxygen

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## Abstract

The catalytic combustion of methane over palladium/zirconia catalyst prepared by oxidation and subsequent reduction of Pd/Zr glassy metals has been investigated with special emphasis on the influence of the catalyst structure (particle size and specific surface area) on the catalytic performance and the impact of a redox mechanism on the product formation. The reaction of 1% methane and 4% oxygen (balance of He) in a fixed-bed microreactor was found to be strongly dependent on the particle size of palladium, which was controlled by appropriate reduction before catalytic testing. Pre-reduction of PdO resulted in an enhanced activity compared to the unreduced catalysts. The structural changes induced upon reduction were accompanied by altered physico-chemical properties, evidenced by different behaviors in the decomposition of PdO and the reduction of PdO by methane. The correlation established between catalytic performance and the rate of reduction of PdO by methane led to the postulation of a redox mechanism, involving the reaction of methane with the active palladium oxide phase and subsequent reoxidation of metallic Pd by oxygen, which was independently confirmed by the use of $^{18}$O labeled catalysts and pulse methods. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Methane oxidation; Palladium/zirconia; Role of lattice oxygen; $^{18}$O labeled palladium oxide

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## 1. Introduction

The effect of pre-reduction on the catalytic activity of supported palladium catalysts for the combustion of methane, generally resulting in an enhanced performance [1–4], is well known but still not fully understood. Reduction of supported palladium oxide causes sintering of palladium [5–11]. Due to a diminished influence of the support, large particles are considered to exhibit higher activity [5]. The increased activity has been further associated with an altered strength of the Pd–O bond [12]. The possibility of a redox mechanism, involving the reaction of methane with lattice oxygen of PdO and subsequent reoxidation of palladium formed, has been proposed to have an influence on the reaction. However, direct experimental evidence for this mechanism is still lacking [1,13–15].

The purpose of this work is to clarify the influence of a possible redox mechanism on the catalytic combustion of methane over palladium oxide supported on zirconia and to relate this influence with structural and physico-chemical changes induced by pre-reduction of the catalyst.

## 2. Experimental

### 2.1. Catalyst preparation

The amorphous Pd/Zr alloys, used as catalyst precursors, were prepared by rapidly quenching the liquid

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melt of the constituents using the melt spinning technique. The resulting ribbons were ground to a powder under liquid nitrogen (200–400 μm). The as-prepared amorphous alloy powders with the nominal composition $Pd_{25}Zr_{75}$ and $Pd_{33}Zr_{67}$ were oxidized (activated) in air in a furnace at 623 K, until full oxidation was accomplished. The resulting $PdO/ZrO_2$ catalyst prepared from $Pd_{25}Zr_{75}$ is referred to as *Pd*, and the catalyst derived from this catalyst by reduction are additionally labeled with the temperature of reduction ($Pd$-$T_{\mathrm{red}}$).

For the preparation of the $^{18}O$ labeled catalysts, the oxidized and subsequently reduced Pd–Zr amorphous alloys were heated with 10°C $\mathrm{min}^{-1}$ to 773 K in an atmosphere containing 30 vol% of $^{18}O_2$ (balance of Ar). After 30 min of reaction at 773 K, the concentration of $^{18}O_2$ was increased to 50 vol% and the sample was kept under these conditions until the pressure did not further decrease, indicating completion of the Pd oxidation (ca. 30 min).

### 2.2. Physico-chemical characterization

X-ray analysis was carried out on a Siemens D5000 powder X-ray diffractometer in a step mode (step size 0.01° and 0.3 s) using Ni-filtered Cu $K_\alpha$ radiation (35 mA, 45 kV). The mean particle size of metallic palladium was calculated from the Pd(1 1 1) reflection using the Scherrer equation with $K$=0.9 and the half-maximum line width correction for Gaussian line profiles.

The specific palladium surface area was determined by CO chemisorption measurements after appropriate reduction of the fully oxidized catalysts. Chemisorption experiments were carried out at room temperature. The specific palladium surface area was calculated assuming a cross-sectional area of 0.0787 $\mathrm{nm}^2$ for the palladium atom and a stoichiometric factor of 2 for the adsorption of CO on palladium. DRIFT investigations of CO adsorption on similarly prepared samples indicated that CO is predominantly chemisorbed as bridge bound CO [16].

The decomposition of PdO of the fully oxidized $Pd_{25}Zr_{75}$ alloy was performed under Ar (30 ml $\mathrm{min}^{-1}$) with a heating rate of 10 K $\mathrm{min}^{-1}$ on a Netzsch STA 409 thermoanalyzer equipped with PtRh10/Pt thermocouples and Pt crucibles. The temperature-programmed reduction of the catalysts (50 mg) with methane was carried out in the microreactor used for catalytic testing with a reduction atmosphere containing 1% methane in a balance of He (total flow 300 ml $\mathrm{min}^{-1}$) and a heating rate of 10 K $\mathrm{min}^{-1}$. The composition of the gas mixture leaving the reactor was analyzed with a mass spectrometer (Balzers GAM 400).

### 2.3. Pulse thermal analysis (PTA)

A Netzsch STA 409 thermoanalyzer was equipped with a pulse device. The thermoanalyzer was further coupled via a heated capillary with a Balzers QMG 420 quadrupole mass spectrometer. PTA (pulse thermal analysis) was carried out isothermally (at 573 and 773 K) or in non-isothermal mode with a heating rate of 4 K $\mathrm{min}^{-1}$ in the range 290–1200 K. Measurements were performed using 80.69 mg of $Pd_{33}Zr_{67}$ after oxidation in air and labeling with $^{18}O$. The volume of injected gas (mixture of methane and oxygen in the ratio 1:4 for catalytic reaction) was 1.0 ml. Argon with a flow rate of 50 ml $\mathrm{min}^{-1}$ was used as a carrier gas.

### 2.4. Pulse measurements and catalytic activity in fixed-bed microreactor

Additional pulse measurements and the catalytic activity tests were carried out in a continuous fixed-bed microreactor (quartz, 4 mm i.d.) operated at atmospheric pressure using a Balzers GAM 400 quadrupole mass spectrometer for gas analysis. The measurements were performed using 100 mg of a fully oxidized $Pd_{33}Zr_{67}$ catalyst for pulse experiments and 320 mg fully oxidized $Pd_{25}Zr_{75}$ catalyst for the catalytic activity testing. For pulse experiments, a volume of 2 ml reaction gas mixture (one part methane (99.995%) and four parts oxygen (99.999%)) was injected into an inert gas flow of 285 ml $\mathrm{min}^{-1}$ helium, which was previously purified by an oxysorb and a hydrosorb column.

The reaction gas mixture for steady state catalytic tests, premixed from pure gases without further purification, consisted of 1% $CH_4$ (99.995%) and 4% $O_2$ (99.999%) in a helium balance (99.998%). Prior to kinetic tests, the catalyst oxidized in air was conditioned in the reaction gas mixture for 1 h at room temperature. After conditioning, the temperature was increased stepwise within a range 450–800 K.

Methane conversion was calculated on the basis of a carbon balance including $CO_2$ and $CH_4$.

Reduction of the oxidized alloy for subsequent catalytic testing was performed by heating the samples in the microreactor under a hydrogen–helium stream (total flow 300 ml $min^{-1}$, 95% He, 5% $H_2$) with 10 K $min^{-1}$ to the respective reduction temperature. The reduced samples were quenched, heated to 623 K under pure He (total flow rate 285 ml $min^{-1}$) and kept at this temperature for 0.5 h. The reduced catalysts were used for catalytic testing without exposing them to the atmosphere.

## 3. Results and discussion

The catalysts prepared by oxidation of the amorphous alloy are made up of intimately mixed domains of palladium oxide and zirconium oxide, as revealed by transmission electron microscopy and electron diffraction. The BET surface area increased upon oxidation from ca. 0.04 to ca. 33 $m^2 g^{-1}$ [17]. Subsequent reduction of the samples at different temperatures allowed us to vary the particle size in a relatively broad range, as illustrated in Fig. 1(a). The increase in the Pd-particle size with increasing reduction temperature was accompanied by a corresponding loss in the specific Pd surface area (Fig. 1(b)). The range of the measured particle sizes is in agreement with data for particle diameters found in [2,3,7,8,10,14,18–20]. Concomitantly to the loss of specific Pd surface area, a diminution of the BET surface area and a shift of the mean pore diameter towards higher values occurred with increasing reduction temperature (not shown). Small pores were eliminated, causing an incorporation of part of Pd from the surface into the bulk.

The chemical behavior of supported palladium oxide is reported to be strongly dependent on the interaction between the palladium phase and the support [1–3,5,9,13–15,17,21,22]. As a result of the enlarged mean particle size, the interface between the palladium phase and the support and thus the influence of the support on the active phase are assumed to become smaller. The changes in the reactivity of PdO of the investigated catalysts are exemplified in Fig. 2 by the course of the decomposition of palladium oxide (Fig. 2(a)) and its reduction by methane (Fig. 2(b)). The unreduced catalyst shows a significant amount of PdO which is decomposed at higher temperatures than the main part of palladium oxide. The first peak appearing at lower temperatures, which is intensified for previously reduced and reoxidized catalysts, is attributed throughout the literature [13,17] to the decomposition of PdO weakly interacting with the support matrix. Similar results have been attained for the temperature-programmed reduction

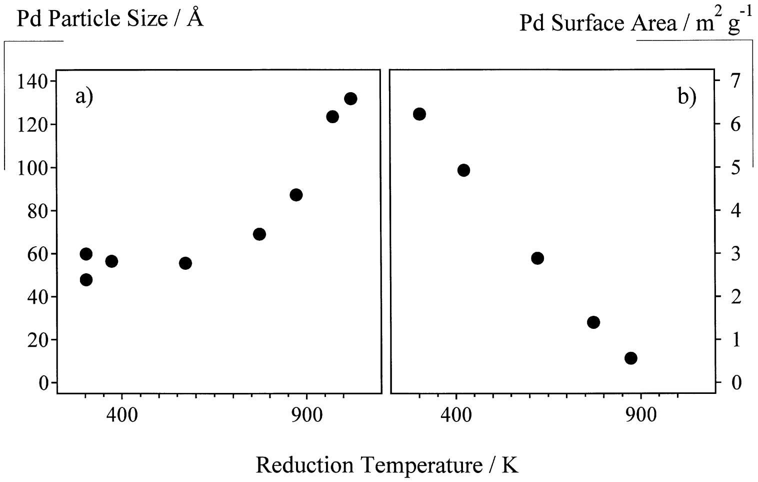


Fig. 1. Textural changes of $Pd/ZrO_2$ catalysts as a function of the reduction temperature. (a) Mean Pd-particle size determined by XRD line broadening (Cu $K_\alpha$) of the (1 1 1) plane. (b) Specific palladium surface area determined by CO chemisorption, $S_{Pd}$=0.0787 $nm^2$; stoichiometric factor, 2.

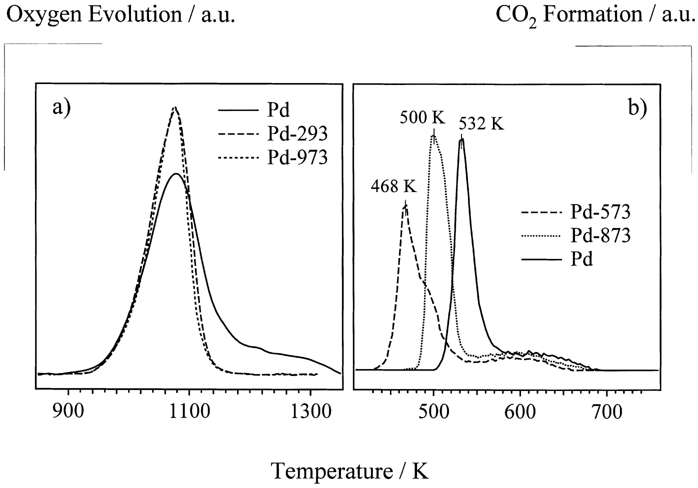


Fig. 2. Change of the reactivity of differently pretreated catalysts. (a) Decomposition of PdO of catalysts reduced at different temperatures (*Pd*-293 and *Pd*-973) and reoxidized and of an untreated catalyst (*Pd*). Conditions: Ar flow rate, 30 ml $\mathrm{min}^{-1}$ (STP); heating rate, 10 K $\mathrm{min}^{-1}$; sample weight, 100 mg. (b) Tempeature-programmed reduction with 1% $CH_4$ in He of an unreduced catalyst (*Pd*) and of catalysts reduced at different temperatures (*Pd*-573 and *Pd*-873). Conditions: total flow rate, 300 ml $\mathrm{min}^{-1}$ (STP); heating rate, 10 K $\mathrm{min}^{-1}$.

by hydrogen of previously reduced and reoxidized catalyst samples (not shown). The altered reducibility of PdO is better resolved using methane as reducing agent. Distinct differences are noticed for catalysts reduced at different temperatures. Comparing the carbon dioxide formation curve of *Pd*-573 and *Pd*-873 and focusing on the shoulder of *Pd*-573 observed in the temperature range of the peak maximum of *Pd*-873, one can assume the existence of several kinds of PdO having different reactivity for the reduction with methane.

In situ reduced catalysts are oxidized upon contact with the reaction atmosphere, containing 1% methane and 4% oxygen, as indicated by a strong exothermicity at room temperature and confirmed by XRD experiments. Therefore, an enhanced catalytic activity observed for previously reduced catalysts compared to the unreduced catalysts, which is visible in Fig. 3(a) for *Pd*-293, *Pd*-573, and *Pd*-873, cannot be traced back to a higher activity of metallic palladium. The varied catalytic performance rather has to be brought in connection with altered properties of the palladium oxide phase after reduction. A comparison of the activity row in dependence of the reduction temperature (Fig. 3(a)) with the ease of reduction of the samples with methane (Fig. 2(b)) indicates a direct link between the rate of reaction of methane with the catalysts and the catalytic reaction. Thus a redox or so-called Mars–vanKrevelen mechanism [23–28], involving the reduction of palladium oxide with methane and the subsequent reoxidation of Pd by oxygen, is proposed according to Scheme 1(c). Since previously reduced catalysts are easily reduced by methane (Fig. 2(b)), the catalytic activity should increase according to the proposed reaction mechanism. The influence of the particle size on the turnover frequency of $CH_4$ is depicted in Fig. 3(b), showing that large particles are more active. The overall performance, however, results from both the specific activity and the number of active sites.

In order to investigate the role of a redox mechanism in the catalytic combustion of methane over palladium-based catalysts, $^{18}O$ labeled catalysts prepared from $Pd_{25}Zr_{75}$ and $Pd_{33}Zr_{67}$ were exposed to pulses of the reaction gas mixture. The oxidation state of the initially fully oxidized Pd-catalysts did not vary during these pulses, as indicated by PTA (monitoring of the weight change). By means of mass spectrometry, reaction product molecules containing $^{18}O$ ($CO_2$ with mass 46 and 48, and $H_2O$ with mass 20) were detected in the pulses after passing through the catalyst bed (Fig. 4). For the first pulse, 20% of the oxygen found in $CO_2$ were $^{18}O$. The amount of labeled $CO_2$ decreased with increasing pulse number as a

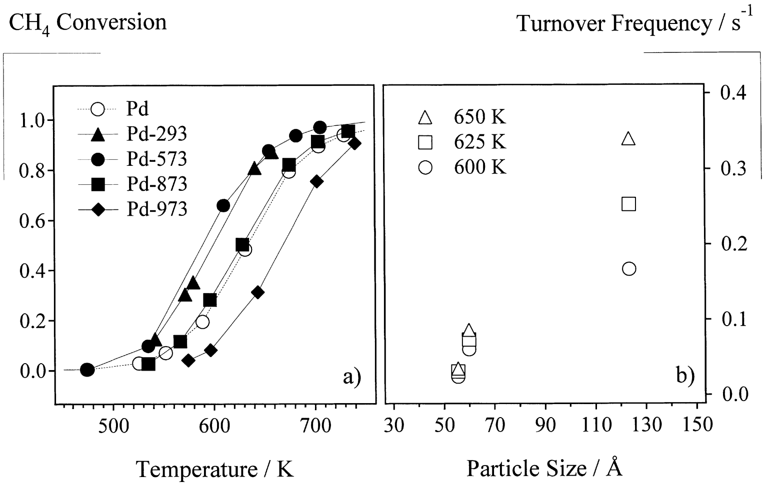
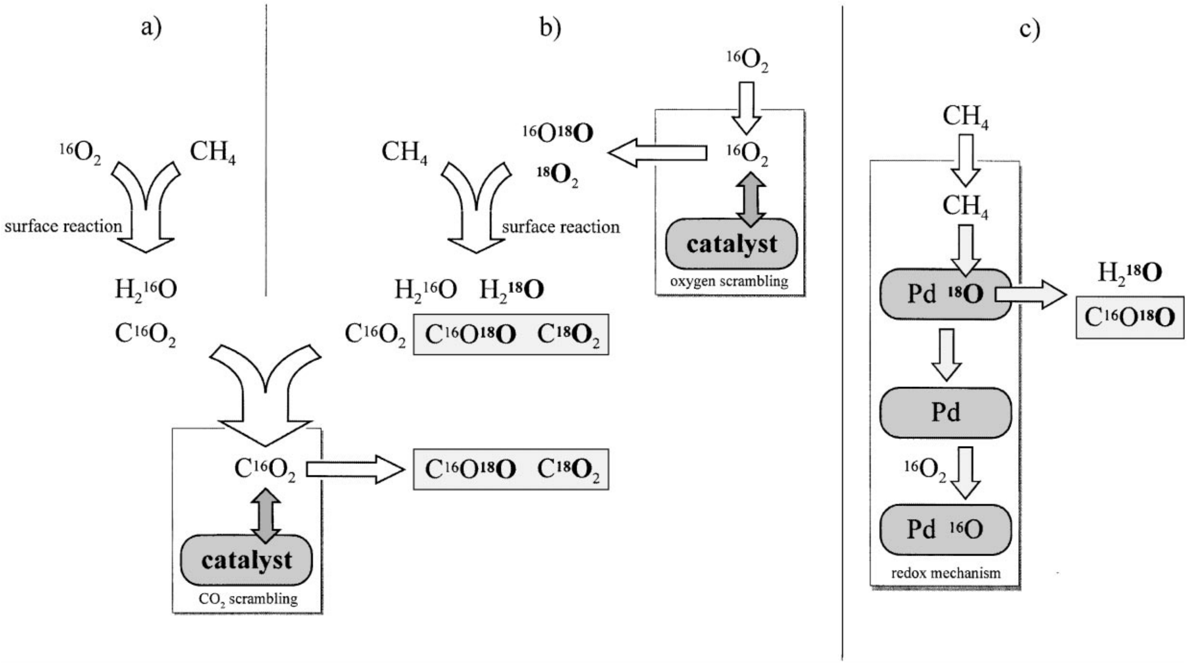


Fig. 3. Influence of the pretreatment and of the Pd-particle size on the catalytic activity. (a) Methane oxidation activities of an unreduced catalyst (*Pd*) and of catalysts reduced at different temperatures. Amount of catalyst is based on 250 mg of amorphous alloy. Reactant gas composition: 1% $CH_4$, 4% $O_2$, He (balance); total flow, 300 ml min$^{-1}$ (STP). (b) Turnover frequency as a function of particle size calculated for different reaction temperatures. TOF calculations are based on the specific surface area measurements (Fig. 1).



Scheme 1. Processes suggested to occur during the contact of the reaction gas mixture with the $PdO/ZrO_2$ catalyst labeled with $^{18}O$. (a) Surface reaction without contribution of a redox mechanism, leading to scrambling of $CO_2$. (b) Scrambling of $O_2$ with the catalyst. (c) Redox mechanism.

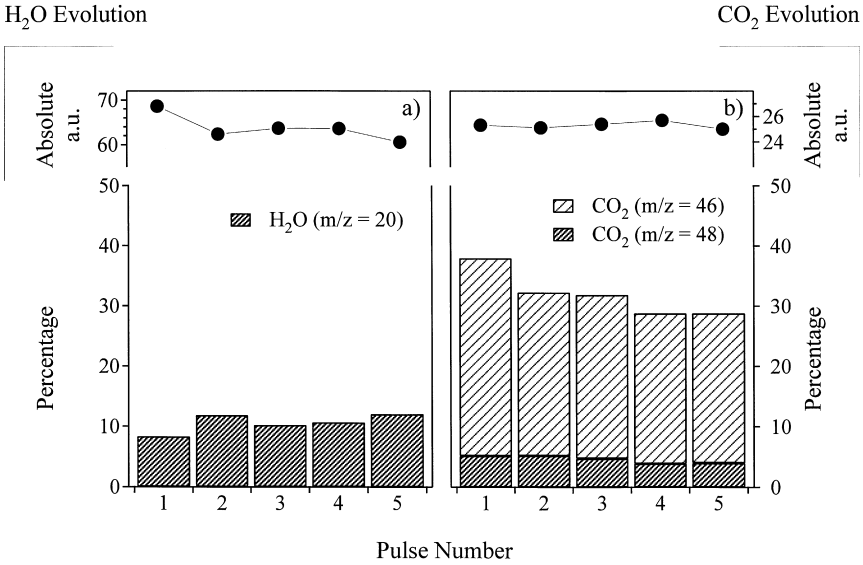


Fig. 4. Change of the gaseous product composition as a function of the pulse number for pulses of the reaction gas mixture (1% methane, 4% oxygen in a balance of Ar) at 573 K: (a) water; (b) carbon dioxide. Conditions: Ar flow rate, 50 ml min$^{-1}$; sample weight, 100 mg.

consequence of the impoverishment of $^{18}$O of the catalyst. A major reason for the rather slow deprivation of the catalyst $^{18}$O has been found in the oxygen diffusion within the PdO phase as well as between PdO and ZrO$_2$. By comparison of Fig. 4(a) and (b), the difference in the relative amount of labeled CO$_2$ and the relative amount of labeled H$_2$O is obvious. This fact might be either an evidence for differences in the scrambling properties of the respective molecules (considerations concerning the oxygen exchange are given below) or a different contribution of a redox mechanism to the formation of the respective product species. The latter would lead to the conclusion that the abstraction of hydrogen atoms from the adsorbed methane species is a normal surface reaction, whereas the formation of oxygen–carbon bonds is more pronounced subjected to a redox mechanism.

The appearance of labeled reaction product molecules in pulses passed over $^{18}$O containing catalysts cannot be explained only by the contribution of a redox mechanism. According to Scheme 1, having a normal surface reaction of the Langmuir–Hinshelwood or Eley–Rideal type, $^{18}$O can be present in product species as a result of scrambling (oxygen exchange) of either molecular oxygen, O$_2$, or CO$_2$. The discrimination between the different sources of $^{18}$O in product molecules is complicated by the simultaneous occurrence of all processes. Since the formation of labeled reaction products by a surface reaction with labeled molecular oxygen proceeds in consecutive steps (oxygen scrambling first produces labeled oxygen, which further reacts to labeled CO$_2$), the fraction of $^{18}$O found in the reaction products cannot substantially exceed the fraction of $^{18}$O in molecular oxygen. For all reaction conditions investigated the amount of $^{18}$O in molecular oxygen is much smaller than the quantity of $^{18}$O found in the reaction products, which allows to preclude a significant contribution of oxygen scrambling.

The effect of CO$_2$ scrambling proved to be of larger importance for the occurrence of labeled products, as revealed by the analysis of the CO$_2$ formation. Pulses of pure CO$_2$ give rise to a considerable exchange of $^{18}$O with the labeled catalyst, represented as the ratio $S_i$ of the signal of $m/z$=46 to the signal of $m/z$=44 (Fig. 5(a)). The lowering of the reaction temperature from 773 to 573 K causes a significant drop of $S_i$. In contrast, the ratio $S_i$ for pulses of the reaction mixture is unaffected by the reaction temperature (Fig. 5(b)). Due to the extent of the CO$_2$ scrambling, the occurrence of a redox mechanism cannot be confirmed for a reaction temperature of 773 K although such a

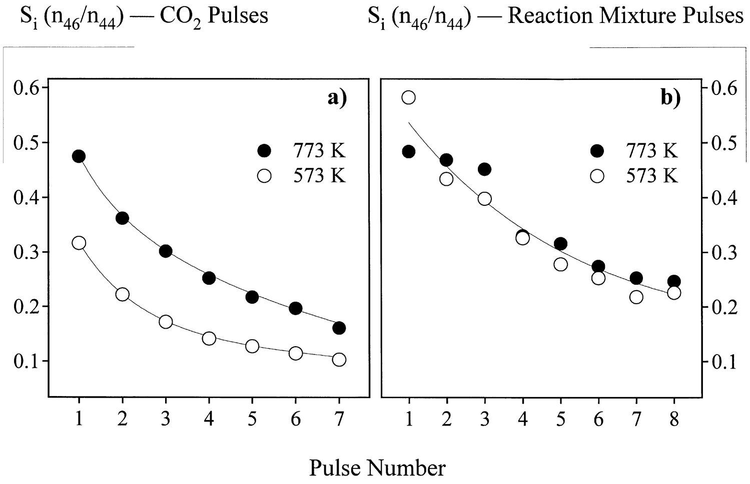


Fig. 5. Effect of the temperature and pulse number on the ratio $S_i$ (definition, see text) upon (a) oxygen exchange of $CO_2$, and (b) reaction of 1% $CH_4$ and 4% $O_2$ in He with an $^{18}O$ labeled catalyst. Conditions: He flow rate, 285 ml min$^{-1}$; pulse volume, 2 ml; catalyst weight, 100 mg; catalysts; 573 K, $PdO/ZrO_2$ prepared from $Pd_{33}Zr_{67}$ precursor; 773 K, $PdO/ZrO_2$ prepared from $Pd_{25}Zr_{75}$ precursor.

mechanism might be possible. However, for a reaction temperature of 573 K, the distinct difference between $S_i$ for $CO_2$ scrambling and for the reaction allows us to attribute the formation of a substantial amount of $CO_2$ to a redox mechanism. A calculation according to Müller et al. [29] reveals at least 20% of $CO_2$ formed to stem from a redox reaction.

The contribution of a redox mechanism explains well the correlation between the catalytic activity and the corresponding physico-chemical properties of the palladium-based catalyst. Since the catalysts initially oxidized consisted of intimately mixed palladium oxide and zirconium oxide domains and thus yielded a strong interaction with the support; pre-reduction of the catalysts before use can result in an enhancement of the catalytic performance compared to the unreduced, freshly activated catalysts. The overall activity is determined by the counteracting influences of the total amount of active sites available and the respective specific activity of these reaction sites, which is related to the contact of the palladium phase with the support. For the catalysts tested, reduction at room temperature or 623 K resulted in best materials for the methane combustion (Fig. 3). Pre-reduction has been found to be a suitable tool for controlling the physical, chemical and catalytic properties of the catalysts. However, the simultaneous loss of specific surface area is a serious disadvantage.

The massive scrambling of carbon dioxide can be explained by a preferential adsorption of $CO_2$ on the catalyst surface. PTA investigation (not shown) revealed the adsorption of $CO_2$ to occur to a much larger extent than the adsorption of $O_2$ and $H_2O$. A possible explanation for the occurrence of a redox mechanism might therefore be the hindered adsorption of oxygen under reaction conditions. The oxidation of adsorbed carbon containing species would have to proceed via the reaction with the oxygen containing catalyst. Although the minimum fraction of $CO_2$ produced via a redox mechanism is set to only 20%, whereas the remaining amount of $CO_2$ may be produced via a normal surface reaction between adsorbed carbon containing species and oxygen, the redox mechanism has to be taken into account when interpreting the catalytic behavior of the catalysts investigated. This reaction pathway is likely to be also relevant for other palladium-based catalysts with different supports.

## 4. Conclusions

The altered catalytic behavior of palladium/zirconia catalysts for the combustion of methane upon reduction has been correlated to physico-chemical changes of the material. Especially the reduction of PdO by methane revealed a decreasing influence of the support with increasing palladium particle size and thus yielded more active catalysts. The proposed redox mechanism, producing $CO_2$ and $H_2O$ via a reaction of methane with the oxidized catalysts followed by reoxidation of the resulting palladium with oxygen, has been confirmed by pulse methods using $^{18}O$ labeled catalysts. Although the analysis was obstructed by the masking influence of oxygen exchange of molecular oxygen and particularly $CO_2$ with the labeled catalyst, the results obtained demonstrate that a redox mechanism influences the performance of palladium/zirconia-based catalysts.

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