# Origins of high activity of Pd/$CeO_2$-based catalysts in methane combustion

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**Abstract:** In comparison with classically prepared Pd/$CeO_2$, such system embedded in porous glasses revealed higher activity for complete methane combustion. The origins of its superior performance were studied by means of steady-state experiments combined with transient tests using isotopic tracers and sophisticated catalyst characterization. In particular, the role of metallic Pd, $PdO_x$, and $CeO_2$ in this reaction was elucidated in detail. Formation of $CO_2$ was established to take place through a Mars-van Krevelen mechanism with participation of lattice oxygen of $PdO_x$ and $CeO_2$. The reaction is initiated by $CH_4$ activation over metallic Pd yielding surface $CH_x$ fragments, which are further oxidized to $CO_2$.

**Keywords:** Methane, Oxidation, TAP.

## 1. Introduction

In the past decades, anthropogenic emissions of methane, a green-house gas with 25-times higher global warming potential than carbon dioxide [1], have significantly increased. Catalytic oxidation of $CH_4$ to $CO_2$ is a promising option for controlling such emissions. However, potential catalytic materials should guarantee a complete conversion of methane at temperatures as low as possible and demonstrate high on-steam stability. Catalysts on the basis of Pd and $CeO_2$ appear to be suitable candidates [2]. Recently, we have demonstrated that supporting of these components on porous glasses (PG) resulted in an active and stable catalyst in comparison with sole Pd/$CeO_2$ [3]. However, fundamental factors responsible for such improvements were not elucidated. To close this gap, the present study was focused on: i) mechanistic aspects of product formation, ii) the role of metallic Pd, $PdO_x$, and $CeO_2$ for activation of oxygen and methane. To this end, we combined steady-state tests and temporal analysis of products using isotopic tracers with catalyst characterization by means of complementary techniques.

## 2. Experimental

Pd/PG, $CeO_2$-PG, and Pd/$CeO_2$-PG were prepared using a porous glass (PG) with an average pore diameter of 151 nm as a support [3]. For comparative purposes, Pd/$CeO_2$ and $CeO_2$ without the glass were also synthesized. The catalysts were characterized by $H_2$-TPR, HAADF-STEM, and CO chemisorption. Steady-state ambient pressure tests were performed in a fixed-bed plug-flow quartz tubular reactor with a feed containing 1 vol% $CH_4$ in air [3]. Pulse experiments with $^{18}O_2$:$CH_4$:Ar=2:1:2, $D_2$:$CH_4$:Ar=1:1:1, or $CH_4$:Ar=1:1 mixtures were carried out in the TAP-2 reactor after catalyst treatment at ambient pressure in $O_2$:$N_2$=1:4 at 350 °C for 1 h, $H_2$:$N_2$=1:1 at 50 °C for 0.5 h, or in vacuum ($10^{-5}$ Pa) at 500 °C.

## 3. Results and discussion

Carbon dioxide was the only carbon-containing product detected in steady-state tests of methane oxidation. The activity of different materials for $CO_2$ formation decreased in the order: Pd/$CeO_2$-PG, Pd/$CeO_2$, and Pd/PG. In order to understand which factors govern the different activity from a mechanistic point of view, pulse experiments with an $^{18}O_2$:$CH_4$:Ar mixture were performed between 250-350°C. $^{18}O_2$ was required for identifying the type of oxygen species (lattice oxygen vs. oxygen from the gas phase), which participate in product formation. The experiments have shown that among the tested catalysts only Pd/$CeO_2$-PG and Pd/PG were active towards methane oxidation. $CeO_2$ and $CeO_2$-PG were not active for methane combustion in the studied temperature range. Similar to the results of steady-state tests, $CO_2$ was the only carbon-containing reaction product. However, the catalyst differed in the pathways of oxygen exploitation as concluded from the different distributions of labelled oxygen in this product. Pd/$CeO_2$-PG oxidized $CH_4$ mainly to $C^{16}O_2$ and marginally to $C^{16}O^{18}O$, i.e. oxygen species in carbon dioxide originated from the lattice of $CeO_2$ and/or $PdO_x$. The ability of latter to oxidize methane was proved in separate pulse experiments with a $CH_4$:Ar mixture. Contrarily to the Pd/$CeO_2$-PG, $C^{18}O_2$, $C^{18}O^{16}O$, and $C^{16}O_2$ were formed over Pd/PG with the main products containing oxygen from gas-phase $^{18}O_2$. Formation of $C^{18}O^{16}O$ and $C^{16}O_2$ was ascribed to fast oxygen isotopic exchange between $^{18}O_2$ and $Pd^{16}O_x$. Importantly, the amount of $CO_2$ formed upon pulsing of an $^{18}O_2$:$CH_4$:Ar mixture significantly decreased after the catalysts were treated in $H_2$ at 50°C or in vacuum at 500°C. No definitive conclusion about the distribution of oxygen in carbon dioxide formed over the Pd/PG catalyst could be drawn due to tiny amounts of this product. The distribution of isotopically labelled oxygen atoms in carbon dioxide formed over reductively treated Pd/$CeO_2$-PG was only slightly changed in favor of $C^{16}O^{18}O$ in comparison to the catalyst treated in an $O_2$:$N_2$ mixture. Hence $CH_4$ oxidation by lattice oxygen of $CeO_2$ is significantly more effective than by adsorbed oxygen species formed from gas-phase oxygen. Summarizing the results of $^{18}O_2$:$CH_4$:Ar pulse experiments, it can be concluded that formation of carbon dioxide over Pd/$CeO_2$-PG and Pd/PG occurs through a Mars-van Krevelen mechanism with participation of lattice oxygen of $CeO_2$ and/or $PdO_x$.

The role of Pd and $PdO_x$ in $CO_2$ formation was studied by pulse experiments with a $D_2$:$CH_4$:Ar mixture. The main attention was paid to the formation of $CH_3D$, which characterizes the activity of the catalyst in breaking the CH bond in $CH_4$. Vacuum-treated ($PdO_x$ was reduced to Pd) Pd/$CeO_2$-PG produced higher amount of this product as compared to Pd/PG (Figure 1). However, the amount of $CH_3D$ formed over oxygen-treated catalysts (both Pd and $PdO_x$ coexist) was even higher. Thus, we can suggest that oxygen species indirectly facilitates breaking the C-H bond in $CH_4$ over metallic Pd yielding surface $CH_x$ species, which is further oxidized to $CO_2$.

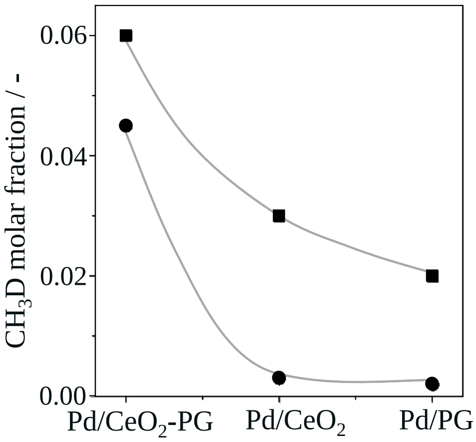

Figure 1. Molar fraction of $CH_3D$ formed upon pulsing of a $D_2$:$CH_4$:Ar = 1:1:1 mixture over (●) $O_2$-treated and (■) vacuum-treated Pd/$CeO_2$-PG, Pd/$CeO_2$, and Pd/PG at 350°C.

## 4. Conclusions

Transient isotopic studies of total methane oxidation over the Pd/$CeO_2$ system demonstrated that lattice oxygen species of $CeO_2$ and/or $PdO_x$ participate actively in the formation of carbon dioxide. This species also indirectly promotes activation of $CH_4$ over Pd particles. Therefore, methane oxidation to carbon dioxide is initiated by $CH_4$ activation on Pd followed by total oxidation of so-formed surface $CH_x$ fragments with participation of lattice oxygen of $CeO_2$ and/or $PdO_x$. Thus, further improvement in the performance of Pd/$CeO_2$-PG catalysts can be achieved by tuning of redox properties of $PdO_x$ species to ensure the presence both of Pd and $PdO_x$ under conditions of methane combustion.

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