

Combined Near-Ambient Pressure Photoelectron Spectroscopy and Temporal Analysis of Products Study of CH₄ Oxidation on Pd/ γ -Al₂O₃ Catalysts

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Natural gas vehicles; CH₄ oxidation; Temporal analysis of products; Near-Ambient Pressure Photoelectron Spectroscopy; Pd active phases; Spill-over;

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Abstract

Vehicles that run on natural gas must be equipped with an exhaust gas after-treatment system to burn their unavoidable CH₄ slip, which must not be released into the environment as CH₄ is a potent greenhouse gas. Pd is known as a highly active catalyst material for CH₄ oxidation. For this study, Pd was deposited on a γ -Al₂O₃ support and the as-received samples were pre-reduced and pre-oxidized, respectively. Near-Ambient Pressure Photoelectron Spectroscopy and the Temporal Analysis of Products methodology were combined to understand that both

electronic states, namely PdO and Pd⁰, are active for the CH₄ oxidation reaction, whereby the superior activity of the pre-reduced Pd/γ-Al₂O₃ catalyst was ascribed to the spill-over of OH-groups from the support to Pd. It was found that the reaction products, CO, CO₂ and H₂, were strongly and, to a large extent, adsorbed on the catalyst surface and were involved in reversible chemical interactions on the catalyst surface during the CH₄ oxidation reaction on the Pd/γ-Al₂O₃ catalyst.

Introduction

Natural gas with a high methane content (> 90%) is growing in public awareness as an alternative fuel to gasoline and diesel due to its low CO₂ emissions per energy content, low NO_x emissions and its practical absence of particulate matter compared to other hydrocarbons. Furthermore, there is major future potential for producing CH₄ on a renewable basis by means of power-to-gas processes [1, 2]. However, as a greenhouse gas, the CH₄ slip being released by vehicles that run on natural gas must be treated catalytically [3] in an on-board exhaust gas after-treatment unit. The CH₄ slip amounts to roughly 5000 ppmv [4-6]. For the emissions control of methane-fueled engines, commercial Ce-Zr-promoted Pd-Rh/Al₂O₃ catalysts (three way catalysts, TWCs), adapted from gasoline engines and designed for stoichiometric fuel to air mixtures ($\lambda=1$), are used [7]. However, the highest efficiency of natural gas engines can be reached under lean burn operation conditions with an excess of oxygen ($\lambda>1$). Accordingly, the periodically-oscillating lean/rich conditions, which are intrinsic to the operation of TWCs, consume additional fuel for effective CH₄ emission abatement and decrease the energetic efficiency. Previous studies by Tompos et al. [8] and Huang et al. [9] show that both metal Pd⁰ and its oxidized form, PdO, can function as active sites for CH₄ activation, whereby PdO is considered the prevailing active phase under oxidizing reaction conditions. It is also stated that an optimum ratio between metallic Pd and PdO species should be set to gain high activity. Kinnunen et al. [10] investigated the dissociation of the C-H bond in CH₄ by means of DFT calculations and found that the coexistence of both phases, Pd⁰ and PdO, is beneficial for the catalytic activity. Bounechada et al. [7] and Fouladvand et al. [11] describe Pd⁰ as only being stable under dynamic oscillating conditions around $\lambda=1$ (change from lean to rich reaction conditions and vice versa) of a gasoline motor and oxidizing to less active, pure PdO particles when switching to the lean burn operation conditions of the engine. As a consequence, the light-off for CH₄ oxidation shifts to higher temperatures, resulting in increasing CH₄ emissions. Against this background, the stabilization of the optimum ratio between metallic Pd and PdO in the exhaust catalyst is a fundamental requirement for establishing highly efficient, lean-burned, natural gas-fired engines.

For an improved understanding of the role of metallic Pd⁰ and PdO during catalytic CH₄ oxidation, transient studies of the physico-chemical interaction between CH₄, the possible reaction products, CO, CO₂, H₂, H₂O, and the catalytic surface of a Pd/γ-Al₂O₃ catalyst using

the Temporal Analysis of Products (TAP) methodology, were carried out in this study. The catalyst was exposed to oxidative and reductive pretreatments, generating well-defined and reproducible electronic states of the Pd species on the catalyst surface prior to its experimental TAP evaluation for CH₄ oxidation. Near-Ambient Pressure Photoelectron Spectroscopy (NAP-XPS) was applied to determine the electronic states of the Pd species following the respective pretreatments and to work out explanatory approaches for potentially different catalytic behaviors. The used Pd/ γ -Al₂O₃ catalyst was synthesized via a colloidal impregnation technique and characterized by N₂ sorption, as well as by Transmission Electron Microscopy (TEM), to determine the particle size of the Pd species. The Pd loading was restricted to 5 wt.%, as is described by Seeburg et al. [4], where higher loadings did not result in significantly improved catalytic activities.

Experimental

Preparation of the Pd/ γ -Al₂O₃ catalyst

The supported Pd catalyst on γ -Al₂O₃ (Puralox TH 100/150 L4, Sasol, Hamburg Germany) was prepared using a colloid adsorption method. In order to be able to observe the changes in the oxidation state of the Pd particles by NAP-XPS in high resolution, the precious metal content was determined as 5 wt.% Pd. For the synthesis of 10 g of the catalyst, 1.22 g of Pd(NO₃)₂ hydrate (Pd content 41 wt.-%, Alfa Aesar) and 1.2 g polyvinylpyrrolidone (K15, Sigma Aldrich) were first dissolved in 100 ml of water and 100 ml of methanol was rapidly added with vigorous stirring. The reaction mixture was then heated under reflux for 0.5 h to complete the colloid generation [12]. In the resulting deep black dispersion, 9.5 g of the γ -Al₂O₃ support was rapidly added. After stirring overnight at room temperature, the obtained black powder was separated from the water as a clear solvent by filtration, thoroughly washed with distilled water, dried overnight at 120 °C and calcined for 2 h in air at a temperature of 550 °C.

Catalyst synthesis and characterization (N₂ sorption and TEM)

The specific surface areas (SSA) of the Pd/ γ -Al₂O₃ catalyst and the γ -Al₂O₃ support were measured by N₂ adsorption at liquid N₂ temperature using the Micrometricis Gemini 2360 system. In order to remove any residual water from the surface, the samples were pretreated overnight at 200 °C under flowing He prior to adsorption. The surface area was then determined using the standard Brunauer-Emmet-Teller (BET) method [13]. Subsequently, the pore size distribution was calculated from the obtained adsorption isotherms in the range of $p/p_0 = 0.05$ -0.95 in accordance with the Cranston-Inclay methodology [14].

To determine the size distribution of the Pd particle on the γ -Al₂O₃ support, Transmission Electron Microscopy (TEM) measurements were carried out using a 200 kV LIBRA 200FE (Carl Zeiss Microscopy GmbH, Oberkochen, Germany) equipped with a high-angle annular

dark-field (HAADF) detector (E.A. Fischione Instruments, Inc., Export, PA, USA), an energy-dispersive X-ray spectroscopy (EDX) apparatus (Bruker AXS GmbH, Karlsruhe, Germany) and a charge-coupled device (CCD) camera (Gatan, Inc., Pleasanton, CA, USA). TEM measurements were performed on the Pd/ γ -Al₂O₃ catalyst and the Al₂O₃ support as a powder, which was dispersed in VE water using an ultrasonic bath and brought onto a carbon-coated copper TEM grid.

NAP-XPS

XP spectra were recorded at room temperature on a Specs NAP-XPS system equipped with a μ -FOCUS 600 X-ray monochromator, an XR 50 MF X-Ray source and a PHOIBOS 150 NAP analyzer before and after the respective catalyst pre-treatments. The Al K α X-ray source (1486.6 eV) was operated at 50 W with a 15 kV anode voltage. The instrument is equipped with an in-situ reaction cell, which allows gas pressures of up to 20 mbar. In order to minimize the charging of the sample, the measurements were performed at 2 mbar Ar. The binding energies of the spectra were referenced to the Al 2p peak at 74.1 eV [15]. The oxidative catalyst pre-treatment was performed with pure O₂ at a pressure of 10 mbar at 400 °C, while the reductive pre-treatment was performed with a mixture of 2.5 mole% H₂ in Ar at a pressure of 10 mbar at 400 °C. The heating of the sample was performed by an IR laser against the backside of the sample holder, with the temperature controlled by a type K thermocouple mounted on the surface of the sample.

TAP

For the TAP experiments, a commercial TAP-KPC reactor system (Mithra Technologies, Inc.) was applied, which can be operated in two different modes. In the commonly called “transient mode”, small gas pulses with pulse widths of between 90-130 μ s were injected into the TAP micro-reactor at ultra-high vacuum conditions, whereas the so-called “flow mode” operates at atmospheric pressure with a constant flow of specific gases for, e.g., pre-treatment purposes. For each experiment, 20 mg of the Pd/ γ -Al₂O₃ catalyst with particle sizes between 200 μ m and 400 μ m were filled into the TAP micro-reactor. For a kinetic experiment using the TAP methodology, three major requirements must be fulfilled from an experimental point of view [16-21]:

- The transport of gases through the catalyst sample is well-defined and only happens as a result of Knudsen diffusion. Gas molecules more likely hit the reactor wall or interact with the catalyst rather than react with one another. Thus, gas phase reactions can be suppressed. As a result, any deviation of the TAP response pulses (e.g., broader or narrower pulses) in comparison to the only Knudsen diffusion case (e.g., using Ar as the internal standard) can be ascribed to the chemical interactions of the respective gas molecules with the catalyst and help shed light on the overall reaction network.

- The active catalytic material is only allowed to slightly change from one inlet pulse to the next (“temporal uniformity”). Such an experiment is considered to be “state-defining”. This means that, experimentally, the number of molecules contained in one inlet pulse is small compared to the number of accessible active sites on the catalyst.
- The third requirement is the “spatial uniformity” of the catalytically-active material. Here, the state of the catalyst, characterized by its surface coverages, must remain uniform within each pulse. By establishing a so-called “thin-zone reactor” concept for which the ratio of the thickness of the catalyst bed to the length of the TAP micro-reactor is in the range of 1/10 to 1/30, the changes to the surface coverages across the catalyst bed are small in comparison to their absolute values.

The “thin-zone reactor” concept was realized by utilizing a catalyst bed with a length of approximately 1 mm, while the total length of the TAP micro-reactor was approximately 34 mm. Hereby, the porosity of the catalyst bed was estimated to be 0.45. Furthermore, by limiting the number of moles of CH₄ per inlet pulse during all experiments to $2\text{--}3 \times 10^{-9}$, the above-mentioned prerequisite of a “state-defining” experiment can be considered fulfilled.

For all TAP experiments in this paper in the transient mode in which CH₄ was involved, the inlet pulses contained 5 mole% CH₄ in Ar. No O₂ was added. The reaction temperature was varied between 100 °C and 500 °C in 50 K intervals. Experiments regarding the single adsorption and desorption of the reaction products CO₂, CO and H₂, respectively, on the Pd/ γ -Al₂O₃ catalyst, were also performed in the transient mode with mixtures of 5 mole% of the respective gases in Ar. The above-mentioned reductive pre-treatment, prior to injecting the CH₄-containing pulses onto the catalyst surface, was performed at atmospheric pressure in the flow mode using a mixture of 2.5 mole% H₂ in Ar at 400 °C for 22 h or pure CH₄ at 400 °C for 20 h, respectively. For the oxidative pre-treatment, pure O₂ at 400 °C for 22 h was fed through the catalyst bed. The pulse responses for CH₄, CO, CO₂, H₂, H₂O and Ar were recorded with a mass spectrometer (Stanford Research Systems RGA 200) at *m/z* values of 16, 28, 44, 2, 18 and 40, respectively.

Results and discussion

Catalyst characterization (N₂ sorption and TEM)

Utilizing Transmission Electron Microscopy, the morphologies of the support and the PdO nanoparticles of the as-received Pd/ γ -Al₂O₃ catalyst after calcination in air at 550 °C were identified. Figure 1 shows the TEM image (left) of the supported Pd/ γ -Al₂O₃ catalyst, which was formed from Al₂O₃ particles with irregular shapes in the range of 15–30 nm. On this γ -Al₂O₃ surface, spherical PdO particles in a size range between 3 and 8 nm were observed (Figure 1, on the right), which are statistically distributed within the pores of the catalyst with a slight tendency towards clustering. The PdO nanoparticles were identified with HAADF-STEM images for the fact that the influence of heavier elements on the image contrast is

stronger, i.e., particles formed by elements with higher atomic numbers appear brighter. In addition, Figure 2 shows, on the left-hand side, a magnified HAADF-STEM image of the Pd/ γ -Al₂O₃ catalyst with an individual, bright particle (tagged with the reticule), whose EDX findings are shown on the right-hand side of the figure. They confirm the presence of O, Al and Pd on the catalyst surface. The measured Cu signal originates from the sample grid material.

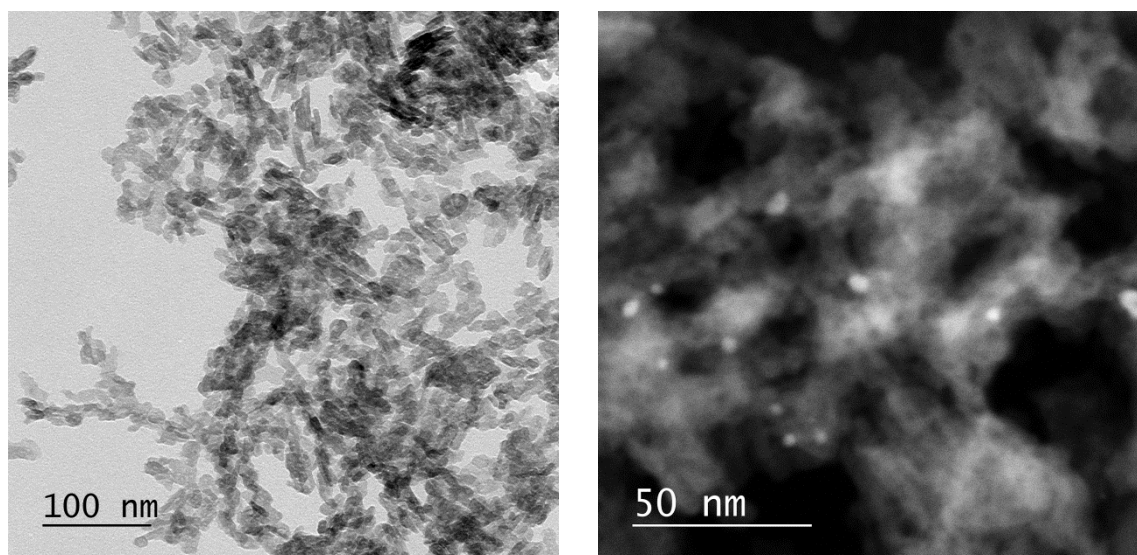


Figure 1 TEM image of the 5 wt.% Pd/ γ -Al₂O₃ catalyst (left) and HAADF-STEM image of the PdO nanoparticles inside the pores (right)

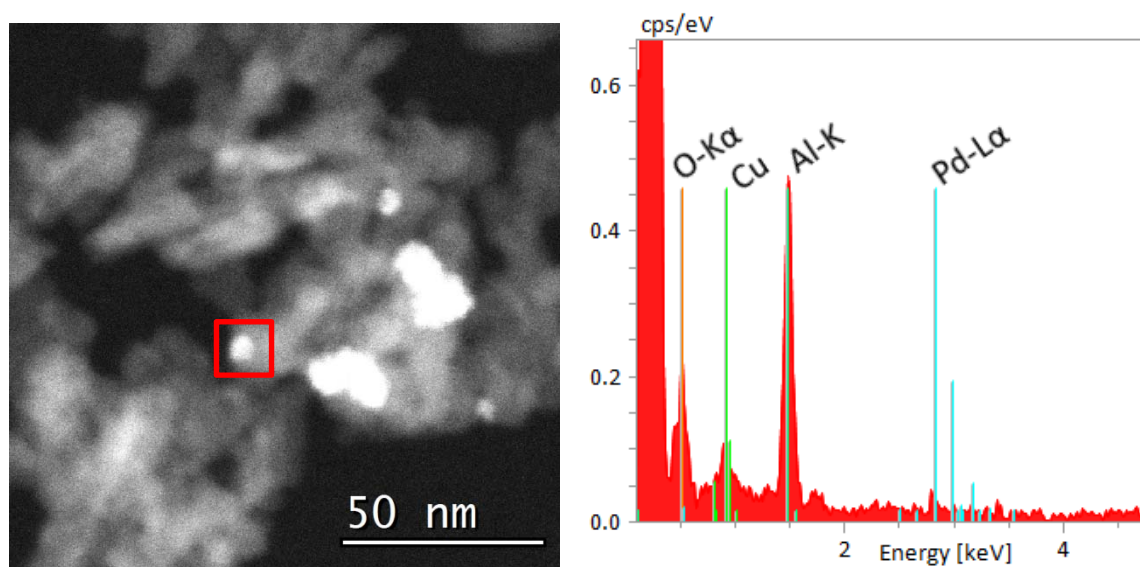


Figure 2 Magnified HAADF-STEM image of the Pd/ γ -Al₂O₃ catalyst (left) with corresponding qualitative EDX findings (right)

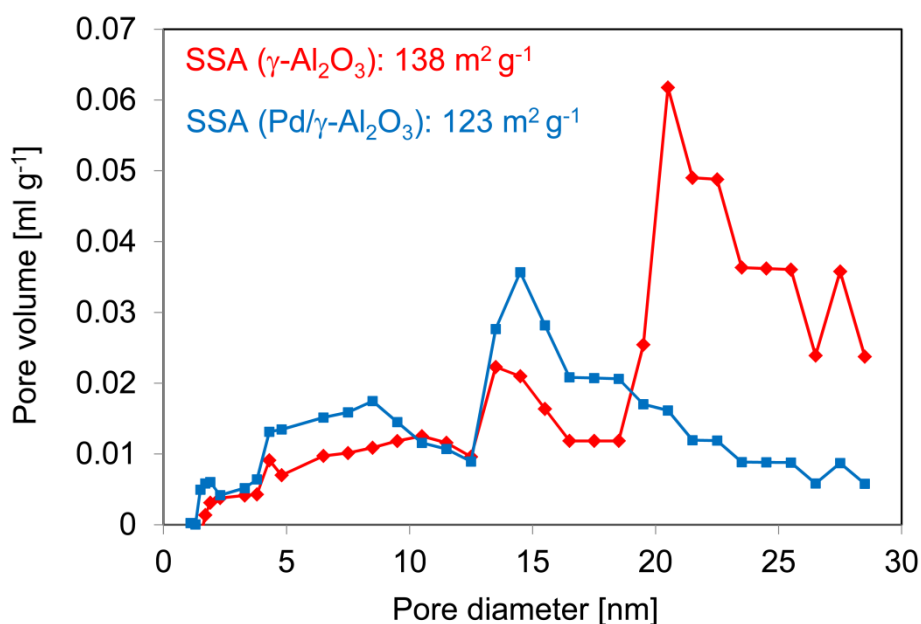


Figure 3 Specific surface areas and pore size distributions of the γ -Al₂O₃ support and the 5 wt.% Pd/ γ -Al₂O₃ catalyst after coating with Pd

The pore size distributions of the γ -Al₂O₃ support and the 5 wt.% Pd/ γ -Al₂O₃ catalyst in Figure 3 reveal that, after precious metal coating, the average pore diameter of the uncoated γ -Al₂O₃ decreased from 22 nm to 15 nm due to the high Pd loading of 5 wt.-%. In addition, a larger amount of smaller pores in the range between 5 nm and 10 nm were formed in the case of the Pd/ γ -Al₂O₃ catalyst, resulting in a total specific surface area of 123 m² g⁻¹, which was only 15 m² g⁻¹ lower than that of the uncoated support.

NAP-XPS

Figure 4 shows the Pd 3d spectrum of the pre-reduced Pd/ γ -Al₂O₃ catalyst (a); and after the oxidative pre-treatment for 2 h (b); and 4 h (c) in accordance with the oxidative pre-treatment procedure described above. Part (a) of Figure 4 shows two asymmetric peaks at 334.8 eV and 340.0 eV, which make up the 3d doublet of metallic Pd⁰ [22-24]. However, already after two hours of oxidative pre-treatment at 400 °C, two additional major peaks appeared at 336.7 eV and 342.0 eV that can be assigned to Pd(II) [24, 25]. The two smaller peaks at 339.6 eV and 344.9 eV are shake-up features that belong to the main oxide species [26]. After a total of four hours with oxidative pre-treatment, the spectrum only shows the peaks belonging to the oxidized Pd species, indicating that the Pd⁰ particles are fully oxidized within the sampling depth of 5-10 nm.

Figure 5 displays the Pd 3d spectrum of an almost fully oxidized Pd/ γ -Al₂O₃ catalyst (a); and after the reductive pre-treatment for 2 h (b) as per the reductive pre-treatment procedure described above. The Pd 3d spectrum of the catalyst in part (b) of this figure only shows the two asymmetric peaks that belong to metallic Pd⁰, indicating that the Pd particles undergo a complete reduction within the sampling depth of 5-10 nm under these reductive conditions. Furthermore, the Al 2p and O 1s regions of the oxidized and reduced catalysts do not display

any changes that could be attributed to the presence of OH-groups on the catalyst surface after the reductive pre-treatment.

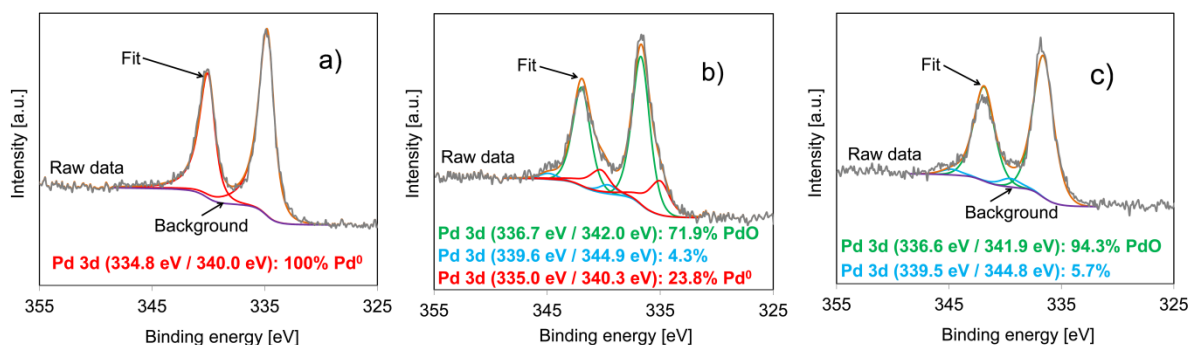


Figure 4 Pd 3d spectrum of the pre-reduced Pd/γ-Al₂O₃ catalyst (a); and Pd 3d spectra after the oxidative pre-treatment for 2 h (b); and 4 h (c) in accordance with the oxidative pre-treatment procedure described above

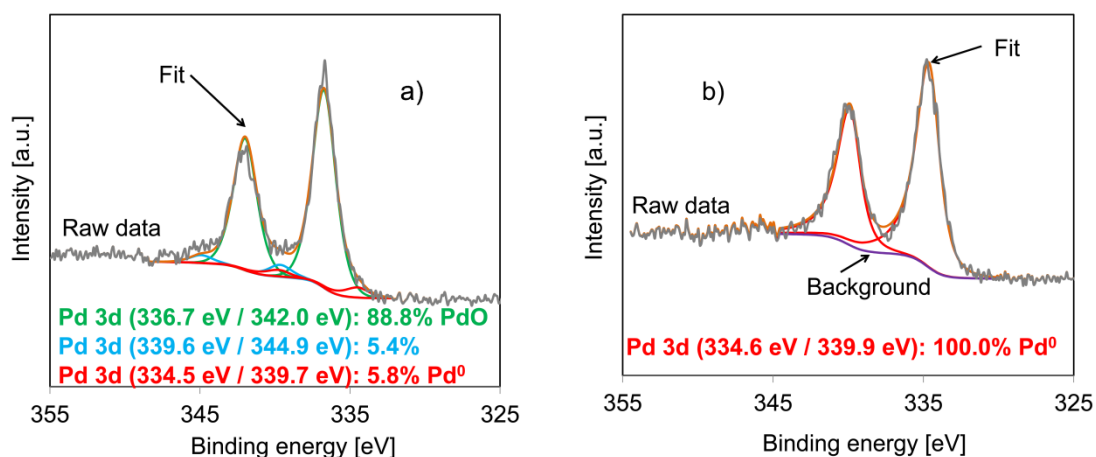
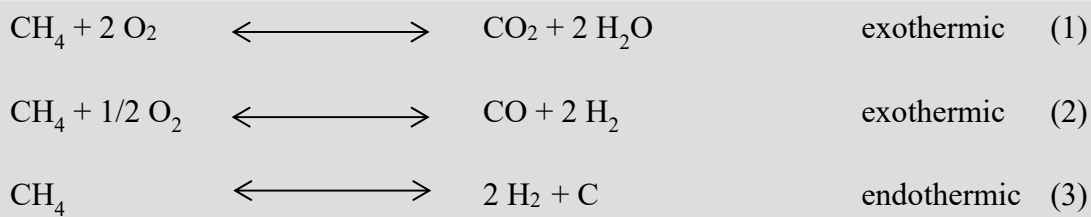


Figure 5 Pd 3d spectrum of an almost fully oxidized Pd/γ-Al₂O₃ catalyst (a); and Pd 3d spectrum after the reductive pre-treatment for 2 h (b) as per the reductive pre-treatment procedure described above

The results from these figures indicate that the oxidative and reductive pre-treatments, as they are described in the experimental section, were highly effective with respect to the formation of the desired well-defined PdO- and Pd⁰-phases, respectively, prior to injecting the CH₄-containing pulses in the TAP experiments.

Temporal Analysis of Products

The experiments displayed in Figure 6 aim to shed light on the adsorption and desorption behavior of the reaction products, CO, CO₂ and H₂, possibly formed in the following reaction equations.



Prior to these experiments, the catalyst was exposed to Ar in flow mode at 400 °C for 30 min. All displayed response pulses of CO, CO₂ and H₂ in Figure 6 were normalized to the Ar signal by multiplying the recorded raw outlet intensities of CO, CO₂ and H₂, respectively, by the ratio of the maximum Ar outlet intensity recorded on inert quartz to the maximum Ar outlet intensity recorded on the Pd/γ-Al₂O₃ catalyst. Furthermore, for the quantification of the percentages of desorbed CO, CO₂ and H₂ molecules as given in Figure 6, not only the zeroth moments of CO, CO₂ and H₂, but also those of the corresponding Ar response pulses were considered.

In the top part, Figure 6 shows, on the left-hand side (a) the response pulses for CO during single adsorption on inert quartz (one average signal calculated from several hundred pulses) and, on the Pd/γ-Al₂O₃ catalyst (one average signal calculated from a series of subsequent 15 pulses) at 200 °C, respectively, after a mixture of 5 mole% CO in Ar has been injected onto the respective samples in transient mode. On the right-hand side (b), the respective results at 400 °C are shown. It becomes evident that at both temperatures, 200 °C and 400 °C, the response pulses for CO on the Pd/γ-Al₂O₃ catalyst were much smaller than those on inert quartz. Quantitatively, at both temperatures, only about 16-17% of the injected molecules could be detected at the outlet of the reactor. This means that CO is adsorbed strongly and, to a large extent, on the Pd/γ-Al₂O₃ catalyst, almost independent of the temperature. These results stand in contrast to those obtained by Kuhn et al. [27] who found CO desorption from differently annealed Pd (111) surfaces at temperatures lower than 275 °C with maxima at approximately 225 °C. However, reproduction experiments could confirm the findings from Figure 6 and also proved that at both temperatures, 200 °C and 400 °C, no CO₂ was produced.

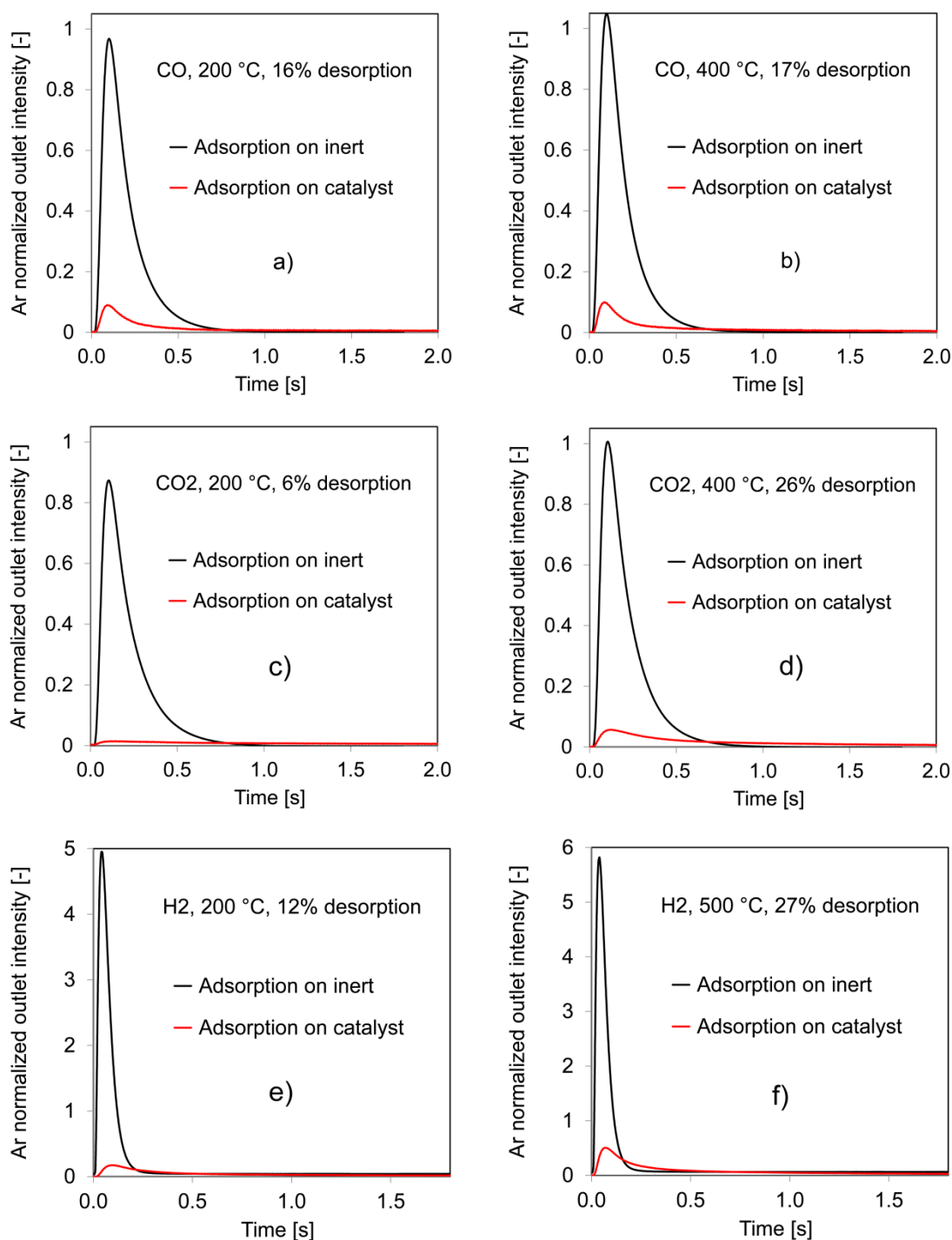


Figure 6 Response pulses in transient mode during single adsorption on inert quartz and the Pd/ γ -Al₂O₃ catalyst for CO at 200 °C (a) and 400 °C (b) from a mixture of 5 mole% CO in Ar, for CO₂ at 200 °C (c) and 400 °C (d) from a mixture of 5 mole% CO₂ in Ar and for H₂ at 200 °C (e), and 500 °C (f) from a mixture of 5 mole% H₂ in Ar

Similar pictures emerge in Figure 6, where the same single adsorption experiments described above were performed with CO₂ (cf. figures (c) and (d)) at 200 ° and 400 °C, respectively, and with H₂ (cf. figures (e) and (f)) at 200 ° and 500 °C, respectively. Also, CO₂ and H₂ adsorbed strongly and, to a large extent, on the surface of the Pd/ γ -Al₂O₃ catalyst. However,

in the case of CO₂ and H₂, a slight temperature effect was observed, leading to stronger desorption from the catalyst surface at 400 °C and 500 °C, respectively. Also in these cases, reproduction experiments could confirm the described findings. They also showed that during the single H₂ adsorption experiments, no H₂O could be detected in the outlet of the micro-reactor by means of mass spectrometry.

The TAP product response pulses in time can be regarded as a residence time distribution in a plug flow reactor. Comparing them qualitatively can yield helpful information about the structure of the entire reaction network. On the one hand, in many cases reaction products involved in reversible processes on the catalyst surface show up later at the exit of the TAP micro-reactor in comparison to residual educts or inert components such as Ar, as they must overcome some kinetic resistance on their way, e.g., the adsorption time scale of the pristine reactant, as well as that of the reaction itself, plus that of their desorption from the surface. These reversible processes lead to a broadening of the response pulses in comparison to the diffusion-only case with Ar. On the other hand, however, if the probability of reacting for educt molecules is different from zero, those educt molecules with a stochastically longer residence time will be more likely to react, whereas those molecules that are able to pass the catalyst bed faster have a far better chance of overcoming the traverse across the catalyst bed. As a consequence, the resulting response pulse for molecules undergoing irreversible processes on the catalyst surface is narrowed in comparison to the diffusion-only case with Ar. With respect to the experiments reported in this paper, Figure 7 presents the normalized outlet intensities as a function of the mass corrected time of CH₄, CO and Ar at temperatures of 100 °C, 150 °C and 250 °C, respectively, on the H₂ pre-reduced Pd/ γ -Al₂O₃ catalyst after a mixture of 5 mole% CH₄ in Ar was injected in transient mode. The normalization of the outlet intensities of the pulses to the same height was performed by simply dividing the values of each curve by its peak value. The mass correction of the time of all response pulses was performed by multiplying the experimentally-recorded time values with the square root of (M_{Ar}/M_{gas}). Here, M_{Ar} stands for the molar mass of Ar and M_{gas} for that of the other gases dealt with in Figure 7. In the CH₄ case, for instance, the recorded time values were multiplied by the square root of (40/16). This mathematical procedure emphasizes how much the different gases are delayed or expedited from their expected values in the diffusion-only case with Ar. It becomes obvious from Figure 7 that, apart from Ar as internal standard and unreacted CH₄, CO formed as per reaction equation (2) was the only product that could be detected in the outlet flow of the TAP micro-reactor at temperatures between 100 °C and 250 °C. Other possible reaction products, such as of H₂, CO₂ or H₂O, were not formed at all or strongly stuck to the γ -Al₂O₃ support under the TAP reaction conditions. CH₄ conversions were significantly high, amounting to 25-50% at these comparatively low reaction temperatures. In Figure 7, in any case the response pulses of CO and unreacted CH₄ were plainly broader than those of Ar. It can be qualitatively concluded from these results that both the molecules, CO and CH₄, were involved in reversible chemical interactions like adsorption

and desorption on the catalyst surface. It is remarkable that at all temperatures between 100-250 °C, the response pulses of CO and CH₄ initially showed a coincident rising part which indicates that at shorter residence times (up to approximately 0.09 s) the desorption of generated CO and unreacted CH₄ molecules took place simultaneously. This finding means that for these cases, the multiple surface steps leading from CH₄ to CO (several C-H bond cleavages and a C-O bond formation) were very fast in comparison with the CH₄ desorption itself and, moreover, in comparison with other slower steps that control the profound tailing of the CO and CH₄ response pulses compared to the diffusion-only case with Ar at residence times longer than 0.09 s. It is interesting to note that, at 100 °C and 150 °C, the tailings of the response pulses of CH₄ were broader than those of CO in the time span from approximately 0.09-0.50 s, while at 250 °C, the curves for CO and CH₄ were very similar also across the time span of the tailing. It can be concluded that in the tailing parts of the respective response pulses, the reversible chemical interactions of CH₄ on the catalyst surface were more complex at low temperatures and low CH₄ conversions (approximately 25%) and became comparable with respect to their extent to those of CO at 250 °C and CH₄ conversions in the range of 50%. Furthermore, in Figure 7, there are temperature-dependent crossing points between the response pulses of CO and CH₄. At 100 °C, the crossing point was at 0.58 s and shifted to 0.41 s at 250 °C. The position of the crossing point is influenced by the number of steps on the surface and the complexity of the reaction network, and is also affected by the magnitude of the rate constants. The exact origin of the relative shape changes as a function of the temperature between CO and CH₄ is beyond the scope of analysis without modeling of the transients. However, the modeling of the transients is not carried out in this paper. The above-mentioned finding, that the response pulses of CH₄ were broader than those of Ar for the diffusion-only case, stands in contrast to the findings of Dhainaut et al. [28], who detected a narrower TAP response pulse for CH₄ compared to that of Ar on their Pd/Al₂O₃ catalyst (2.5 wt% Pd), indicating irreversible processes on the catalyst surface in this case.

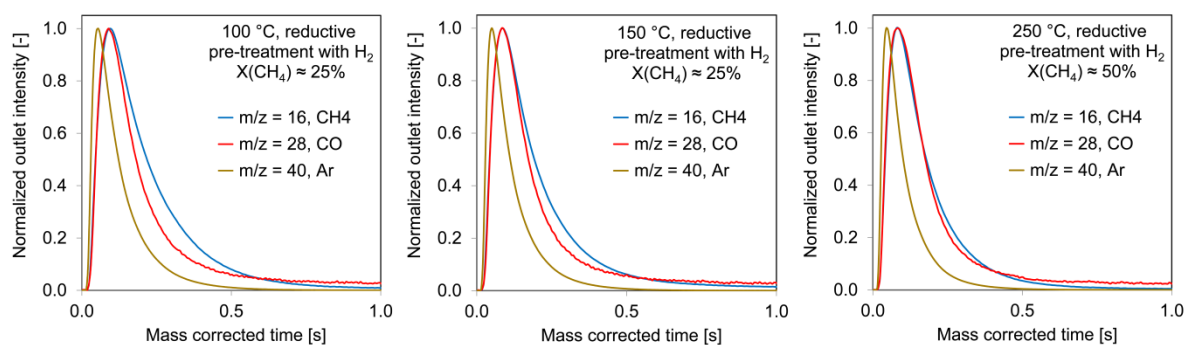


Figure 7 Normalized outlet intensities in transient mode as a function of the mass corrected time of CH₄, CO and Ar at temperatures of 100 °C, 150 °C and 250 °C, respectively, on the H₂ pre-reduced Pd/γ-Al₂O₃ catalyst from a mixture of 5 mole% CH₄ in Ar

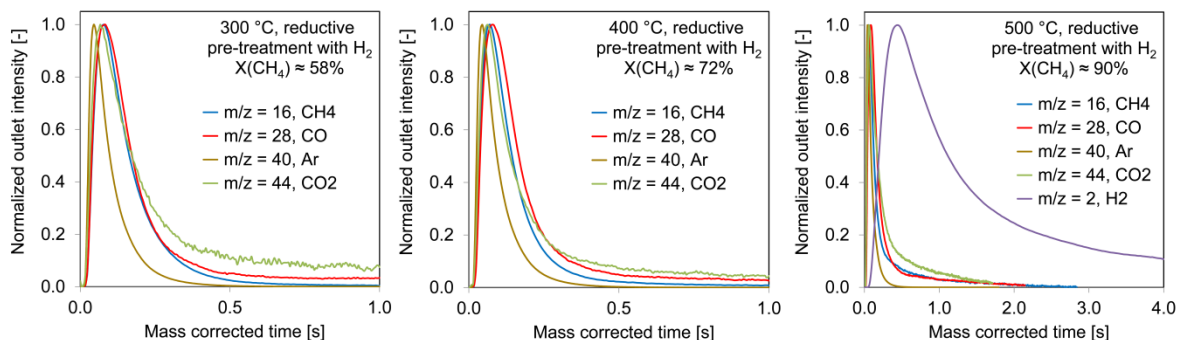


Figure 8 Normalized outlet intensities in transient mode as a function of the mass corrected time of CH₄, CO, CO₂, H₂ and Ar at temperatures of 300 °C, 400 °C and 500 °C, respectively, on the H₂ pre-reduced Pd/ γ -Al₂O₃ catalyst from a mixture of 5 mole% CH₄ in Ar

As a continuation of the experiments shown in Figure 7, Figure 8 presents the normalized outlet intensities in transient mode as a function of the mass corrected time of CH₄, CO, CO₂, H₂ and Ar at temperatures of 300 °C, 400 °C and 500 °C, respectively, on the H₂ pre-reduced Pd/ γ -Al₂O₃ catalyst. The figure shows that although the results from Figure 5 prove that the reductive H₂ pre-treatment led to fully reduced Pd particles on the catalyst surface prior to injecting the CH₄-containing pulses, CO as well as CO₂ (according to reaction equation (1)) were detected as oxidation products in the outlet flow of the micro-reactor at temperatures above 300 °C. Parallel to the commencing formation of CO₂, the conversion of CH₄ increased from approximately 58% at 300 °C to about 90% at 500 °C. These experimental findings require the ability of the Pd/ γ -Al₂O₃ catalyst to supply oxidative reagents for the observed oxidation reactions, in which the activation of CH₄ by dissociative adsorption is considered the first step [29-31]. As the NAP-XPS measurements proved only elemental Pd⁰ due to the reductive H₂ pre-treatment, only the γ -Al₂O₃ support comes into question in this respect. Schuurman et al. [32] found that for CH₄ reforming with CO₂, Al₂O₃ supports this reaction via the inverse spill-over of OH-groups to the Ru active phase. Wang et al. [33] investigated the partial oxidation of CH₄ on a Rh/Al₂O₃ catalyst. They observed that H₂O, which was adsorbed on Al₂O₃, can supply O-atoms for the oxidation reaction via the inverse spill-over of H₂O or OH-groups onto Rh particles. Heitnes Hofstad et al. [34] also report on spill-over processes from their supports to the Rh-active phase during the partial oxidation of CH₄ to syngas. These explanations, which comprise inverse spill-over processes from the support to the precious metal to help activate CH₄, can be adduced to explain the enormous oxidative capability of the reductively pre-treated Pd/ γ -Al₂O₃ catalyst described in this paper, although the NAP-XPS measurements did not provide experimental evidence for the OH-groups. It could be that the concentration of OH-groups was below the detection limit of the NAP-XPS apparatus used for the experiments in Figure 4 and Figure 5.

The right-hand part of Figure 8, which displays the response pulses recorded on the H₂ pre-reduced Pd/ γ -Al₂O₃ catalyst at 500 °C, shows a very broad signal for H₂. Dhainaut et al. [28] found similarly broad response pulses for H₂ at 400 °C when they investigated CH₄ dissociation on a pre-reduced Pd/Al₂O₃ catalyst and ascribed it to slow H₂ spill-over processes from the metal to the Al₂O₃ support. A similar process was reported by Ren  me et al. [35]. In their study, Cavanagh and Yates [36] investigated H₂ spill-over on a Rh/Al₂O₃ catalyst whose synthesis also featured a final step of reduction with H₂. They used infrared spectroscopy to examine the exchange of D₂ with OH-groups chemisorbed onto the Al₂O₃ support. They conclude from their experiments that the spill-over process comprises several single steps, i.e., the fast dissociation of D₂ to Rh particles, the fast transition of the dissociated D-atoms to the Al₂O₃ support, the slow migration of H-atoms across the Al₂O₃ support and, finally, the fast replacement of H-atoms in the OH-groups by “spilled-over” D-atoms. However, on pure Al₂O₃ without Rh loading, the exchange of H-atoms by D-atoms was not observed as the initial step, i.e., the dissociation of D₂ on Rh could not take place. Wang et al. [37], on the contrary, offer as an explanation for broadened H₂ response pulses with their Rh/Al₂O₃ catalyst that H₂O adsorbs on the Al₂O₃ and spills over onto Rh, where it dissociates, forming H₂ and leaving adsorbed O-atoms and OH-groups on the metal. A different and perhaps subsidiary explanation for the broadening of the H₂ response pulse in Figure 8 on the right-hand side at 500 °C is the slow dehydrogenation of CH₄, forming H₂ and carbon-containing species on the catalyst surface. To shed light on the question of whether CH₄ dehydrogenation is relevant, the pre-reduced Pd/ γ -Al₂O₃ catalyst was titrated with a large number of pulses containing even 50% CH₄ in Ar. It was found that after 8250 pulses, the H₂ pulse responses became significantly smaller and remained constant, while in parallel the CH₄ signals became much larger. Furthermore, at the end of this series, no further CO or CO₂ molecules could be detected in the outlet flow. This means that the catalyst lost its oxidative capability and it was concluded that only the above-mentioned dehydrogenation still took place at the end. In this respect, Figure 9 shows the averaged CO₂ response pulse that was detected when the CH₄-titrated Pd/ γ -Al₂O₃ catalyst was exposed to inlet pulses containing 50% O₂ in Ar at a reaction temperature of 500 °C. The detected CO₂ outlet intensity in Figure 9 is much higher than those that were found in the experiments outlined in Figure 8. This clearly indicates that the catalyst surface was strongly covered with carbon-containing species as a consequence of the long titration sequence and offers clear experimental evidence that CH₄ dehydrogenation according to reaction equation (3) is an important part of the reaction network on the pre-reduced Pd/ γ -Al₂O₃ catalyst at temperatures in the range of 400-500 °C. The coverage of the catalyst surface with carbon-containing substances can also explain that CH₄ oxidation, forming CO and CO₂, was no longer possible after the titration series due to catalyst deactivation.

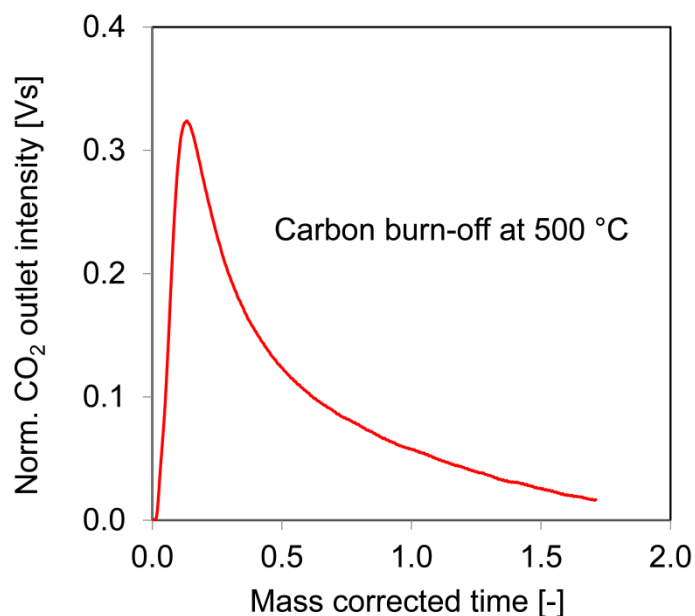


Figure 9 Outlet intensities of CO₂ in transient mode as a function of the mass corrected time at 500 °C after the pre-reduced Pd/γ-Al₂O₃ catalyst was titrated with a mixture of 50% CH₄ in Ar

In order to be able to differentiate whether the delay of the H₂ molecules at the exit of the TAP micro-reactor associated with the broadening of the H₂ response pulse in Figure 8 is due to the above-described spill-over of H₂ from Pd to the Al₂O₃ support or to the observed slow dehydrogenation of CH₄, or even to both processes, an additional experiment was run, during which a mixture of solely 5 mole% H₂ in Ar was pulsed on the surface of the pre-reduced Pd/γ-Al₂O₃ catalyst at 500 °C in transient mode. Figure 10 compares the obtained response pulses of H₂ and Ar with those for the CH₄ oxidation reaction at the same temperature of 500 °C. It can be seen that the Ar response pulses representing the diffusion-only cases through the catalyst bed were fairly comparable, with only slight differences. However, a significant broadening of the H₂ response pulses occurred when H₂ alone was pulsed on the catalyst. Thereby, no H₂O formation was observed. According to the literature [28, 35, 36], this pulse shape can be ascribed to H₂ adsorption on the Pd and spill-over to the Al₂O₃ support. It is interesting to note that in this figure, significant additional delay and broadening of the H₂ pulse response was observed in the case of the CH₄ oxidation reaction, which can be attributed to the slow dehydrogenation of CH₄ on the pre-reduced Pd/γ-Al₂O₃ catalyst at 500 °C, as was described above. This means that both processes, H₂ spill-over and CH₄ dehydrogenation, are responsible for the broad H₂ response pulse in Figure 8 and Figure 10.

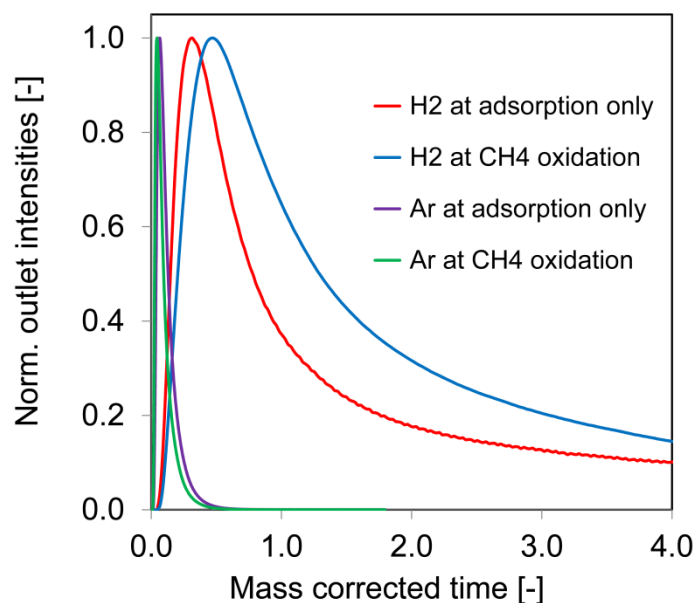


Figure 10 Outlet intensities of H₂ and Ar in transient mode as a function of the mass corrected time during H₂ pulsing alone and, during the CH₄ oxidation reaction, with inlet pulses containing 5 mole% CH₄ in Ar on the pre-reduced Pd/ γ -Al₂O₃ catalyst at 500 °C

The product formations in time at different reaction temperatures as described in Figure 7 and Figure 8 for the H₂ pre-reduced Pd/ γ -Al₂O₃ catalyst were similar in the cases of the pre-oxidized and CH₄ pre-reduced catalysts. The most apparent differences were found with respect to the formation of H₂. On the CH₄ pre-reduced Pd/ γ -Al₂O₃ catalyst, this was more pronounced and even took place at temperatures of 400 °C and higher, while it was not observed at all at any temperature in the case of the pre-oxidized sample. It is also noteworthy that for none of the experimental series at different reaction temperatures – regardless of the catalyst pre-treatment (H₂ pre-reduced, CH₄ pre-reduced or pre-oxidized) – H₂O formation was observed. Renème et al. [31] explain the lacking of H₂O response pulses in their experiments by the very slow desorption of H₂O and the fast re-adsorption on the Pd and/or on the Al₂O₃ support.

Although the pre-treatment procedure did not have a decisive influence on the product formation in time, it is interesting to note whether CH₄ conversion was affected. In this respect, Figure 11 shows the Ar-normalized CH₄ outlet intensities in transient mode as a function of the mass-corrected time at different temperatures on the pre-oxidized and H₂ pre-reduced Pd/ γ -Al₂O₃ catalyst. As it was experimentally found that the outlet intensity of any response pulse even increases when simply the temperature in the micro-reactor rises, the CH₄ outlet intensities must be Ar-normalized if they are to be quantitatively compared. Ar normalization means that the recorded CH₄ outlet intensities at a specific temperature are multiplied by the ratio of the maximum Ar outlet intensity at the maximum reaction temperature to the Ar outlet intensity at the specific reaction temperature. This calculation guarantees that the observed differences in the CH₄ outlet intensities are only due to

interactions with the catalyst. Figure 11 shows that for both pre-treatments, a clear influence of the reaction temperature on the intensities of the CH₄ response pulses was detected. In both cases, they were highest at 100 °C and continuously decreased when the reaction temperature increased, indicating increasing CH₄ conversions with rising temperatures. It is interesting to note in this figure that the CH₄ outlet intensities on the H₂ pre-reduced catalyst were lower at all temperatures compared to those of the pre-oxidized catalyst. This resulted in CH₄ conversions of between 0-10% at low temperatures and 70-80% at high temperatures in the pre-oxidized case and between 20-30% at low temperatures and 75-90% at high temperatures in the case of pre-reduction with H₂. The respective estimates for the apparent activation energies amount to $\approx 20 \text{ kJ mole}^{-1}$ for the reductive pre-treatment with H₂ and $\approx 37 \text{ kJ mole}^{-1}$ for the pre-oxidation case. These values, however, are in contrast to those found by Ciuparu et al. [3] on a Pd catalyst, which were higher in the case of pre-reductive pre-treatment. From the results of Figure 11, it can be concluded that both Pd phases, Pd⁰ and PdO, are highly active for CH₄ oxidation in the absence of O₂ in the educt mixture, especially at reaction temperatures of between 400-500 °C. However, these data also suggest that an O₂-rich Pd surface is slightly less active for CH₄ oxidation than a reduced Pd⁰ phase onto whose surface OH-groups spilled over from the Al₂O₃ support as it was described by different groups [32-34]. Maestri et al. [38] performed a micro-kinetic analysis of steam and dry reforming of CH₄ on Rh catalysts and conclude from their study that OH-groups are more efficient oxidizing reagents than O-atoms. However, there is no clear picture in the literature whether high O₂ coverage is beneficial for the CH₄ oxidation reaction. Wang and Liu [39] report in their DFT study that PdO is the active phase for CH₄ activation on a PdO/HZSM-5 catalyst, and Maillet et al. [40] report lower apparent activation energies and higher CH₄ conversions on a pre-oxidized Pd/ γ -Al₂O₃ catalyst (1 wt.% Pd). However, other groups found that the dissociative adsorption of CH₄ is suppressed when the catalyst surface reveals high coverage with O-atoms [41-44].

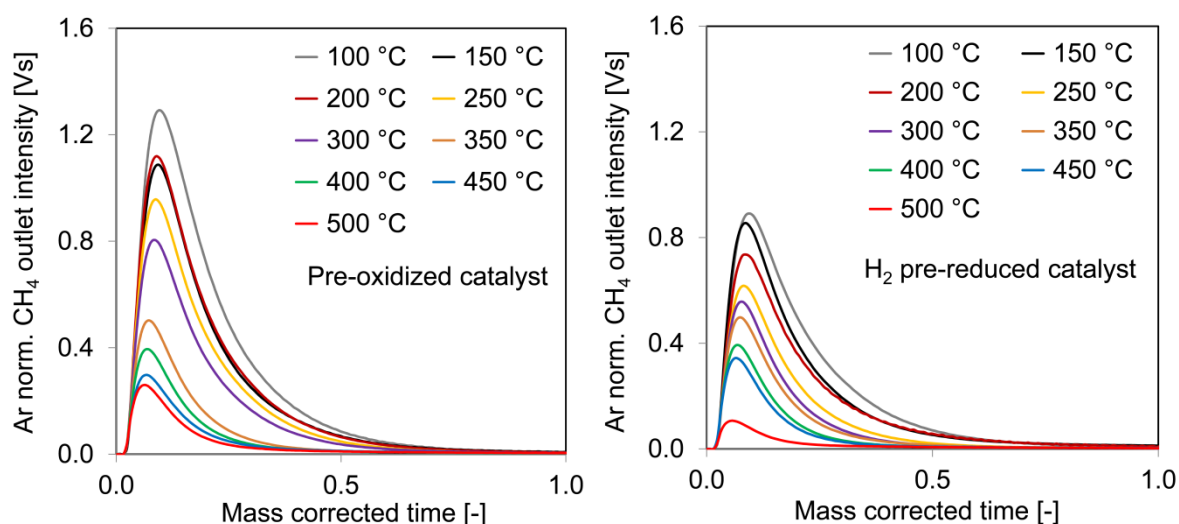


Figure 11 Ar-normalized CH₄ outlet intensities in transient mode as a function of the mass corrected time at different temperatures: on the pre-oxidized Pd/ γ -Al₂O₃ catalyst (left) and the H₂ pre-reduced Pd/ γ -Al₂O₃ catalyst (right)

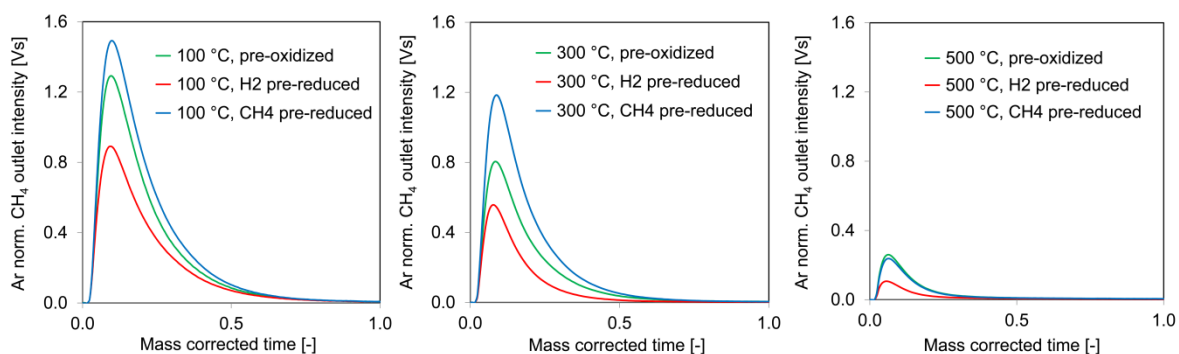


Figure 12 Ar-normalized CH₄ outlet intensities in transient mode as a function of the mass corrected time depending on the pre-treatment procedure of the Pd/ γ -Al₂O₃ catalyst: at 100 °C (left), 300 °C (middle) and 500 °C (right)

As a complement to Figure 11, Figure 12 shows the Ar-normalized CH₄ outlet intensities in transient mode as a function of the mass corrected time depending on the pre-treatment process of the Pd/ γ -Al₂O₃ catalyst at 100 °C, 300 °C and 500 °C, respectively. This figure once again shows that the pre-reduction of the Pd/ γ -Al₂O₃ catalyst with H₂ led to the lowest CH₄ outlet intensities and thus the highest CH₄ conversions at all three reaction temperatures. The new aspect of this figure, however, is that at each reaction temperature, the CH₄ outlet intensities of the CH₄ pre-reduced catalyst were significantly higher than those in the case of pre-reduction with H₂. The conclusions deduced from the findings in Figure 9 (coverage of the catalyst surface with carbon-containing substances after exposure to CH₄ at elevated temperatures) can be transferred to explain the results in Figure 12. The pre-reduction of the Pd/ γ -Al₂O₃ catalyst with CH₄ at 400 °C will also have led to CH₄ dehydrogenation and the formation of carbon-containing deposits on the catalyst surface, which are known to reduce the catalytic activity by at least partially blocking the catalytically-active sites.

Conclusions

The CH₄ oxidation reaction has been scientifically investigated for many years, as it is a suitable route for significantly reducing the quantities of environmentally-harmful CH₄ released by vehicles that run on natural gas. For the investigations reported in this paper, Pd/ γ -Al₂O₃ was chosen as the catalyst, as Pd is known from the literature to be highly active when initiating CH₄ dissociation, which is considered the first step of CH₄ oxidation. NAP-XPS measurements could confirm that well-defined electronic states of the Pd phase, PdO and Pd⁰, were set by oxidative (flow of pure O₂) and reductive (flow of H₂ in Ar) pre-treatments of the Pd/ γ -Al₂O₃ catalyst prior to injecting pulses of CH₄ onto the catalyst surface. TAP experiments revealed that both PdO and elemental Pd⁰ were highly active for the conversion of CH₄, especially at temperatures of between 400-500 °C, with CH₄ conversions being in the range between 70-90%. Thereby, the H₂ pre-reduced catalyst was even slightly more active than the pre-oxidized sample. It was concluded that the promising catalytic activity of the elemental Pd⁰ species was only made possible by highly efficient oxidizing OH-groups that spilled over from the Al₂O₃ support to Pd and favored the activation of the C-H bond in CH₄, whereas the slightly lower catalytic activity of the PdO phase was ascribed to high coverage of the catalyst surface with O-atoms that hindered dissociative CH₄ adsorption. Nevertheless, it is beneficial for the applicability of the Pd/ γ -Al₂O₃ catalyst in exhaust gas after-treatment units that it properly works under reductive and oxidative conditions. Future work will aim to further investigate the optimum ratio between PdO and Pd⁰ and how it can be experimentally set. On the reduced surface of the Pd/ γ -Al₂O₃ catalyst, slow CH₄ dehydrogenation at 500 °C was observed that constitutes a possible risk of catalyst deactivation, as the catalytically-active sites could be blocked by carbonaceous deposits. Furthermore, the TAP experiments revealed that the reaction products CO, CO₂, and H₂ adsorbed strongly and, to a large extent, on the catalyst surface in the whole temperature range between 100-500 °C and were, as CH₄, involved in complex and reversible interactions with the catalyst surface. The role of H₂O in the reaction network could not be elucidated, however, as it was not detected in the TAP experiments. Although it must have been formed, it obviously fully stuck to the Al₂O₃ support under the TAP reaction conditions.

Acknowledgements

The authors would like to thank the BMWi for financial support of the NAP-XPS set-up (03ET1460A).

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