Deep oxidation of methane on particles derived from YSZ-supported Pd-Pt-(O) coatings synthesized by pulsed filtered cathodic arc.

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Abstract

Methane conversion tests were performed on Pd, PdO\textsubscript{y}, Pd\textsubscript{0.6}Pt\textsubscript{0.4}O\textsubscript{y} and Pd\textsubscript{0.4}Pt\textsubscript{0.6}O\textsubscript{y} thin films deposited on yttria stabilized zirconia (YSZ) substrates. Pt containing films exhibited poor activity and high reducibility. As-deposited Pd and PdO\textsubscript{y} films showed good activity and transformed, during the cycling process, to particles dispersed on the YSZ substrates. The higher reaction rate of initially PdO\textsubscript{y} films was explained by a better dispersion of the catalyst. A drop of the reaction rate was observed when the temperature exceeded 735°C and 725°C for initially Pd and PdO\textsubscript{y}, respectively, which can be associated with the high-temperature reduction of PdO into Pd.

1. Introduction
Improving the efficiency for the catalytic combustion of methane (CH\textsubscript{4}) represents a challenge for the reduction of working temperature of CH\textsubscript{4} combustion turbines. Palladium catalysts have been shown to belong to the most effective catalysts for methane combustion (e.g. [1–6]) and to be more active than other transition metals for this reaction [5,7,8]. While bulk PdO is claimed to be inactive, a thin layer of PdO on metallic Pd is proposed to be the active form of palladium [8-10]. It was suggested that CH\textsubscript{4} combustion occurs via the Mars–van Krevelen mechanism where O\textsubscript{2} is assumed to oxidize the palladium surface, the formed surface oxide being reduced by CH\textsubscript{4} [4]. A bifunctional mechanism for methane oxidation over Pd/ZrO\textsubscript{2} catalysts has already been suggested, where metallic Pd particles dissociatively chemisorb methane producing adsorbed H and CH\textsubscript{X} species [8,10]. Reoxidation rapidly converts the metal back to the oxide. The predominance of either metallic palladium-supported PdO or a Pd/PdO\textsubscript{y} mixture for active oxidation of methane is still highly controversial. For Al\textsubscript{2}O\textsubscript{3} support, the incorporation of Pt in Pd has been reported to improve and stabilize the catalytic oxidation of methane via Pd-Pt interaction (e.g. [12, 13]). On the contrary, Persson et al. observed superior conversion efficiency for Pd than Pd-Pt equimolar mixture, the latter presenting higher long term stability [14].

Pulsed Filtered Cathodic Vacuum Arc (PFCVA) can be successfully employed to deposit various chemical systems such as diamond like carbon (DLC), metal doped DLC [15, 16] and metal oxide [17, 18] films. The high reactivity of the evaporated species associated with the technique and the use of a dual cathode deposition system (DC-PFCVA) is expected to lead to the successful synthesis of binary and ternary noble metal oxide films. In the present study, yttria stabilized zirconia (YSZ) supported Pd-based catalysts were considered due to the applicability of YSZ.
supports to solid oxide fuel cells and car engine exhausts where electrochemical
promotion of catalysis start being considered [19, 20]. This study presents DC-
PFCVA as a suitable technique to synthesize various metallic or oxide thin films for
catalytic reactions, and explores the thermal evolution of the catalytic activity for YSZ-
supported metallic Pd, Pd oxides and Pd$_{x}$Pt$_{1-x}$ oxides.

2. Experimental

2.1. Sample preparation

Metallic Pd, Pd oxide and Pd$_{x}$Pt$_{1-x}$ oxide films were prepared on YSZ pellets (14
mm in diameter, 1 mm thick). The system contains a dual-cathode “triggerless” mini-
gun [21], which was designed to operate in pulsed mode. The two cathodes
incorporated in the source were pure palladium and platinum. The pulsed operation
of these cathodes was controlled using a custom National Instruments’ LabView™
software. Once the computer has sent a signal to the arc power supply, an arc
discharge pulse on a selected cathode is triggered simply by application of a high
open circuit voltage (of about 600 V). The pulsed arc current employed was about
700 A with a pulse duration of about 1 ms. A pulse repetition rate of four pulses per
second was employed for all films. The two mixed Pd$_{1-x}$Pt$_{x}$O$_{y}$ films were deposited
by alternating one platinum pulse and one palladium pulse for the higher Pt-
containing Pd$_{1-x}$Pt$_{x}$O$_{y}$ film, and one platinum pulse for every two palladium pulses for
the lower Pt-containing Pd$_{1-x}$Pt$_{x}$O$_{y}$ film. The plasma stream produced by the mini arc
source was injected into a 90-degree filter to remove most of the macroparticles,
90-degree filter, the plasma stream travelled through a magnetic multipole homogenizer with 16.7 cm inner diameter in order to improve the film uniformity [22]. The substrate holder was grounded and rotated at a rate of 2 revolutions per minute during the deposition. The distance between the exit of the filter to the homogenizer was about 3 cm, and the distance from the magnetic homogenizer to the substrate was about 2 cm. The vacuum base pressure was typically in the $10^{-4}$ Pa range, the process pressure was set at approximately 2.13 Pa (16 mTorr). For the deposition of the pure palladium film, pure Ar was used as process gas while for the deposition of the oxide films pure oxygen was introduced to the chamber at 16 standard cubic centimeters per minute. The films were deposited at the same time on cubic YSZ pellets and silicon wafer pieces.

2.2. Sample characterization

The structural characteristics of the films were probed by grazing incidence X-ray diffraction (GIXRD) at an incident angle of 2° with respect to the substrate surface. The experiments were done with a Co-Kα source (wavelength of 0.178897 nm) using an INEL diffractometer. The film composition was measured by secondary neutral mass spectrometry (SNMS) with an 8 keV Ar$^+$ primary beam. The apparatus is a SimsLab-VG. The typical currents on the samples were in the range 300-500 nA and the sputtered atoms were post-ionised by the electrons emitted from a filament for the mass spectrometry analysis. The quantification procedure of the relative Pd and Pt content and the estimate of the oxygen content of as-grown films included, first, a calibration of the SNMS measurements using thick crystalline Pt$_2$O and PdO sputtered reference films, as well as SNMS measurements of a thick Pd$_{0.85}$Pt$_{0.15}$O$_y$
film whose metals stoichiometry was previously determined by energy dispersive spectroscopy (EDS). The compositions of thin catalyst films where then deduced from the integration of the SNMS profile corrected using the calibration. The surface of the Pd-based catalysts was observed by scanning electron microscopy (SEM, XL30S FEG Philips). Thickness measurements were carried out with a Dektak IIA profilometer on films deposited on flat silicon substrates.

Catalytic measurements were performed at atmospheric pressure in a specific quartz reactor described in a previous study [23, 24]. The catalysts were placed on sintered quartz, 18 mm in diameter. The reactive mixture passed through the porous disk from below and then licked the catalyst surface. A K-type thermocouple was located close to the catalytic surface. The reaction gases were mixtures of CH\textsubscript{4} (Air Liquide, 5% CH\textsubscript{4} in He) and O\textsubscript{2} (Air Liquide 5% O\textsubscript{2} in He). The gas composition was controlled by mass flow controllers (Brooks, with accuracies better than 1%). In the following, the gas composition will be expressed in ppm or %. The reactive mixture (RM) is containing CH\textsubscript{4}/O\textsubscript{2}: 5100 ppm/4%. The overall gas flow rate was kept with He constant at 72 mL min\textsuperscript{-1} (+/- 2 mL min\textsuperscript{-1}). To study the catalytic performance and the thermal ageing, three cycles were performed between 250°C and 800°C at a ramp of 10°C min\textsuperscript{-1} with a plateau of two hours at 800°C for each sample. The comparisons between catalytic surfaces of Pd, PdO, and Pd\textsubscript{x}Pt\textsubscript{1-x}O\textsubscript{y} were performed during cycling. The reactants and products were analysed by an IPC400TM INFICON quadrupole mass spectrometer. Signals at m/e = 15, 18, 28, 32, 44 amu corresponding to CH\textsubscript{3}+, H\textsubscript{2}O+, N\textsubscript{2}+ or CO+, O\textsubscript{2}+ and CO\textsubscript{2}+ ions, respectively, were recorded. The conversion of methane was defined as the percentage of methane
feed converted into CO$_2$. Carbon dioxide was the only oxidation product detected. The catalytic rate was calculated in reference to the palladium loading.

3. Results and discussions

Some characteristics concerning catalytic coatings are reported in Table 1. The as-deposited Pd films were found to be nanocrystalline with an average grain size of about 10 nm while all the oxide films were amorphous. SEM examination of the samples revealed a complete coverage of the YSZ surface by the deposited materials with a dense morphology. While palladium oxide, PdO, and platinum dioxide, PtO$_2$, are stable in air at low temperatures, they start reducing in air at around 750°C [7] and 450°C [25], respectively. The estimated oxygen content in the as-deposited films (y) decreases with the incorporation of Pt. The methane conversion curves of the deposited films upon heating after a first RT-800°C-RT (RT: room temperature) thermal cycle are displayed on Fig. 1a. The Pd, Pd$_y$O coatings promote methane deep oxidation upon heating below 770°C whereas the promotion by the Pd$_{0.6}$Pt$_{0.4}$O$_y$ film stops at roughly 750°C. The highest conversions occurred for as-deposited Pd and Pd$_y$O films. Very low catalytic activity is observed on Pd$_{0.4}$Pt$_{0.6}$O$_y$ film. The present results are in accordance with the detrimental effect of Pt incorporation into Pd$_{1-x}$Pt$_x$ for $x \geq 0.33$ reported by Persson et al. for the same reaction [14].

For a better comparison of the different catalysts, the reaction rate has been calculated in reference to the palladium loading (Fig.1 b). The representation highlights a superior catalytic activity of as-deposited palladium oxide films compared
to metallic palladium. The behavior of Pd$_{0.6}$Pt$_{0.4}$O$_y$ is characterized by lower activity
between 580°C and 680°C. This might be related to the onset of the reduction of
oxidized platinum. In this context, it is worth noting that Seriani et al. calculated a
higher efficiency of platinum oxide (Pt$_3$O$_4$) than Pt for CH$_4$ cracking [26]. We believe
that the strong platinum reducibility explains the improved reducibility of the
compound, leading to a reaction rate drop at 680°C for Pd$_{0.6}$Pt$_{0.4}$O$_y$ and of the
negligible activity for Pd$_{0.4}$Pt$_{0.6}$O$_y$.

The thermal cycling behavior of the as-deposited Pd and PdO$_y$ films is shown in
Fig. 2. Starting from metallic palladium, the onset of the catalytic conversion is
observed at 550°C upon the first heat up, whereas PdO$_y$ is already active at 400°C.
The reaction rate drops at 735°C and 725°C for initially Pd and PdO$_y$ films,
respectively. These temperatures cause the reduction of PdO into metallic Pd. They
are higher than the 700°C reported in oxidizing mixtures by Furuya et al. for Pd
nanoparticles on YSZ [27], and the 715°C reported by Roche et al. for 52-nm thick
Pd thin films sputter-deposited on YSZ [28]. Cooling down the samples from 800°C,
surface re-oxidation occurs, thereby restarting the conversion the hydrocarbons.
However, the reoxidation of the surface occurs at a lower temperature than the
reduction upon heating. Both materials exhibit an activity hysteresis of about 100°C.
The phenomenon is qualitatively consistent with the original observation by Farrauto
et al. for Al$_2$O$_3$-supported Pd [7]. The thermal cycling of PdO$_y$ did not give any
evidence for strong differences between the cycles. In the case of Pd, the first
heating is associated to a lower activity. This indicates a strong structural or/and
chemical evolution of the Pd film during the first heating. From the previous
discussion, the reducibility of the compounds drives the thermal evolution of the
catalytic activity. Palladium was the only crystalline as-deposited film. The GIXRD
signature of the different samples after the third cycle is represented on Fig.3. These investigations interestingly highlight that the final structural state is very sensitive to the initial composition:

- The only phase detected for Pt-containing films is metallic (no Pt oxide).
- The as-deposited Pd film transformed into a biphased alloy consisting of Pd and PdO.
- The as-deposited PdOy film converted into crystalline PdO. The reddish colour characteristic of PdO could be observed only for that sample.

Therefore, the hypothesis of the higher reducibility of Pt-containing films is confirmed. The SEM observation of both initially Pd and PdOy films shows an important evolution of the morphology towards clusters of particles dispersed at the surface of the zirconia substrate (Fig. 4). PdOy evolved in jagged clusters of few particles with a characteristic size of the particles close to 100 nm. The clusters derived from the Pd film are bigger and more spherical in shape. Significant coalescence occurred between the particles. The differences in shapes and sizes are linked to strong differences in the surface to volume ratio. Using a spherical approximation for the particle shape, the dispersion of the catalyst was estimated to 6 and 16 % for initially Pd and PdOy films respectively. Assuming a surface oxidation for both compounds within the thermal domain of active heterogeneous catalysis, the latter parameter obviously explains the discrepancy between the maximal activities of the two compounds.

Conclusions
Methane conversion tests were performed on Pd, PdO$_y$, Pd$_{0.6}$Pt$_{0.4}$O$_y$ and Pd$_{0.4}$Pt$_{0.6}$O$_y$ thin films deposited by Dual Cathode Filtered Cathodic Vacuum Arc on YSZ substrates. The catalytic activity curves over thermal cycling were discussed in terms of the reducibility of the deposited compounds. The film with the highest Pt content exhibited poor activity and Pd$_{0.6}$Pt$_{0.4}$O$_y$ showed limited activity and high reducibility. In contrast, during the cycling process, the as-deposited Pd and PdO$_y$ films showed good activity despite the transformation to clusters of particles dispersed on the YSZ substrates. The higher reaction rate of the initially PdO$_y$ films was explained by a better dispersion of the catalyst. The drop in the reaction rate, associated with the reduction of PdO into Pd at high temperature, was measured at 735°C and 725°C for the initially Pd and PdO$_y$ films, respectively. After three thermal cycles up to 800°C, it was not possible to detect either Pd or Pt oxides in the Pt containing films. As-deposited Pd evolved to a Pd/PdO mixtures, only crystalline PdO was detected for initially PdO$_y$ amorphous films.

Acknowledgments

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References


[22] A. Anders, Cathodic Arcs: From Fractal Spots to Energetic Condensation. New
York: Springer, 2008


Table 1: Some characteristics of the deposited catalysts. * As-deposited.
Figure captions

Figure 1: Methane conversion a), methane reaction rate in reference to the Pd load b) over the deposited compounds during the second heat up from 250°C to 800°C.

Figure 2: Evolution of the methane reaction rate during thermal cycling.

Figure 3: X-ray diffraction patterns of the deposited compounds after thermal cycling.

Figure 4: PdO particles derived from thermally cycled PdO$_x$ films deposited films a), mixed PdO + Pd particle clusters derived from thermally cycled Pd films deposited films b).
Figure 1a

The graph shows the CH₄ conversion [%] as a function of temperature (°C). Different materials are represented with different symbols and line styles:
- Black squares: Pd
- Green inverted triangles: PdO_y
- Red circles: Pd₀.₆Pt₀.₄O_y
- Blue triangles: Pd₀.₄Pt₀.₆O_y

The CH₄ conversion increases with temperature, reaching a peak at around 700 °C for all materials except PdO_y, which shows a different trend.
Figure 1b

The figure shows the reaction rate of \( \text{CH}_4 \) [mol s\(^{-1}\) g\(^{-1}\) Pd] as a function of temperature [°C]. The graph compares the reaction rates for different compositions of Pd and Pt in O\(_y\). The reaction rates are represented by different line styles and markers for each composition:

- Pd
- PdO\(_y\)
- Pd\(_{0.6}\)Pt\(_{0.4}\)O\(_y\)
- Pd\(_{0.4}\)Pt\(_{0.6}\)O\(_y\)
Figure 2
Figure 3

The graph shows the diffracted intensity [arb. units] as a function of the diffraction angle (degrees). The peaks corresponding to PdO, Pd, and Pt are indicated. The substrate is YSZ, and the samples are labeled as Pd$_{0.4}$Pt$_{0.6}$O$_y$, Pd$_{0.6}$Pt$_{0.4}$O$_y$, and PdO$_y$.
<table>
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<th>Composition</th>
<th>Initial structure</th>
<th>Thickness (nm)</th>
<th>Oxygen/Metal (y) *</th>
<th>Pd loading (μg)</th>
<th>Final structure (3 cycles)</th>
<th>Maximal catalytic rate (mmol CH₄ s⁻¹ g⁻¹ Pd)</th>
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<td>/</td>
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