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ORIGINAL PAPER

Electrochemical promotion of deep oxidation of methane on Pd/YSZ

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Abstract Electrochemical catalysts based on Pd deposited by Physical Vapour Deposition on YSZ were used for methane deep oxidation. Different thicknesses of Pd films varying from 11 to 75 nm were catalytically characterized between 150 and 750 °C. The Pd loadings were extremely low. Catalytic and EPOC experiments were carried out on those electrochemical catalysts. Their catalytic activities were compared with the performances of a reference catalyst. It was found that the catalytic activity can be in situ tuned by applying an anodic polarization thus supplying oxygen ions at the surface of the catalyst. Faradaic efficiency values up to 258 were observed and the induced modifications of the catalytic rate were typically 100 times higher than the corresponding ionic current. The influence of the polarization on the temperature of decomposition of the palladium oxide was also examined. The polarization was found to enhance the thermal stability of the oxide and turn palladium oxide into metallic palladium at higher temperatures.

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1 Introduction

Natural gas is a major source of thermal energy. Palladium-based catalysts have the highest catalytic activity for the deep oxidation of methane (DOM). DOM on Pd catalysts depends on the chemical state of palladium. Though previous work [1] has shown that palladium oxide is the active phase, other work [2] has reported that the coexistence of palladium oxide and metallic palladium exhibits the best activity. However, the deactivation of Pd based catalysts limits their use in high temperature catalytic reactors. It is suggested [3] that deactivation at high operating temperatures is closely linked to the thermodynamic transformation of PdO in metallic Pd and the concomitant particle sintering. This study aims at electrochemically promoting the DOM over Pd catalysts by using electrochemical promotion of catalysis (EPOC) or also called Non-Faradaic Electrochemical Modification of Catalytic Activity (NEMCA) [4]. Practically, the reaction was carried out on an electronically conducting and porous film of Pd interfaced with a solid electrolyte pellet, oxygen ion conductor. An inert counter electrode was deposited on the other side of the solid electrolyte support to form an electrochemical catalyst in a galvanic cell. The concept introduced and developed by Vayenas et al. [4] is based on the application of low currents or potentials through the catalyst/electrolyte interface to modify the catalyst activity, in a reversible manner. EPOC is related to the migration of ions from the solid electrolyte to the surface of the catalyst upon polarization. The spillover of ions under polarization was demonstrated using different characterization techniques by Vayenas et al. [4]. Recently Janek et al. used spectroscopic experiments [5] on Pt/YSZ electrochemical catalysts to show that the oxygen ions are formed at the three phase boundaries. They clearly observed the mobility of spillover species on the catalyst film which is also predicted by the model of Leiva [6] for a metal deposited on a sodium conductor.

The induced modification of the activity due to the presence of ions at the surface of the catalyst is expected to be superior to the electrochemical rate of supplied ions or ionic current. The resulting catalytic rate increase is pronounced and exceeds that predicted by the Faraday's law. Indeed, a single ion could activate the reaction of more than one gaseous adsorbed molecule. The supply or the removal of the promoting ions modifies the binding energy of the reactants on the catalyst. The theory suggested by the group of Vayenas on the origin of EPOC is the variation of the catalyst work function by the polarization. EPOC has been investigated up to now on more than 50 reactions and on different catalysts such as (Pt, Pd, Rh…) [4, 7] or oxides such as IrO_2 [8], or perovskite oxides [9, 10] deposited on a large number of ionic conductors such as YSZ, NASICON, Nafion, and recently potassium conductors [11]. Two major parameters are commonly used to describe a NEMCA effect: the rate enhancement ratio (ρ) of CO_2, defined by

$$\rho = \frac{r}{r_0} \tag{1}$$

where r_0 is the catalytic reaction rate of CO_2 production under open circuit conditions and r is the reaction rate under polarization. The Faradaic efficiency Λ is also defined to quantify the magnitude of the promotion induced by the polarization,

$$\Lambda = \frac{r - r_0}{\frac{I}{nF}} \tag{2}$$

where I is the current, n the number of charge carried by the ions and F the Faraday's constant.

Electrochemical promotion of methane has already been investigated on Pt/YSZ by Tsiakaras and Vayenas [12]. Under anodic polarization, the catalytic rates were found to increase independently of the CH_4:O_2 ratio. Due to the high operating temperatures, the observed rate enhancements were restricted and the measured Λ values were quite low (up to 3) whereas ρ values were found to be up to 70. Electrochemical promotion of methane has already been shown on Pd catalyst for ethylene oxidation [13, 14] and NO reduction by carbon monoxide [15, 16]. The authors reported rate enhancements ratio values up to 4. Only a few studies are available concerning the DOM on Pd/YSZ. Athanasiou et al. [3] reported a reaction rate increase under anodic polarization when supplying O^{2-} ions from YSZ to the surface of the catalyst. The maximum rate enhancement observed was 4 times higher than the ionic current at 650 °C for an applied potential of +1 V under stoichiometric conditions. The reported Faradaic efficiency values were quite low due to the high operating temperatures (650–750 °C) and consequent short lifetime of the promoting species and important part of the non catalytic homogeneous reaction. Another study [17] focused on a lower temperature range (350–450 °C) and reported higher average lambda values around of 100 and ρ values up to 90. Frantzis et al. [13] found quite similar faradaic efficiency values typically between 30 and 150. In the present study, the influence of anodic polarization on methane deep oxidation was investigated on sputtered Pd/YSZ electrochemical catalysts containing low palladium loadings in excess of oxygen at 500–600 °C. For the first time the feasibility of EPOC on very thin Pd films with very low Pd loadings deposited on YSZ for methane deep oxidation was reported. The goal of the study was to discuss the impact of the presence of oxygen ions (anodic polarization) on the oxidation of methane. The PVD films exhibited a high activity per gram of catalyst compared with classical painted films. Hence, this study reports a comparison of the performance of electrochemical catalysts with very low Pd loadings with an industrial catalyst. Finally this paper demonstrates for the first time the benefit of the anodic polarization on the transition temperature of palladium oxide to metallic palladium.

2 Experimental

Electrochemical catalysts were based on thin Pd films deposited on dense solid electrolyte pellets i.e. 8 mol% Y_2O_3-stabilized ZrO_2 (YSZ), 17 mm in diameter and 1 mm thick. The YSZ solid electrolytes were prepared from a TOSOH powder 99.99%, with an average grain size of 0.3 µm, sintered at 1,350 °C for 2 h to obtain a densification superior to 98%. YSZ is an oxygen ion conductor at the operating temperatures of the study. Pd films were deposited on the ionic conductor by PVD (Physical Vapour Deposition) technique. The experimental device, described elsewhere in details [18, 19] is a 40 L sputtering chamber pumped down via a secondary oil diffusion suction system allowing a base vacuum of about 10^{-4} Pa. A MKS Baratron pressure gauge was used to measure the total pressure. The argon partial pressure was fixed at 0.3 Pa. This parameter influenced the porosity of the prepared films [7, 20]. The target was 50 mm diameter and was powered by an advanced energy dc supply equipped with a fast arc detector able to cut microarcs within 1–2 µs. The discharge current was maintained at a constant level of 0.2 A. Films of different thicknesses were deposited by varying the deposition time. The thicknesses of the coatings were determined by analysing the transmittance-wavelength curves measured with a Varian Cary 5000 optical spectrometer thanks to a programme developed by PVDco Ltd. [21, 22] using a similar layer deposited on a glass substrate. Before depositing the Pd layers by PVD on one side of the electrolyte, gold counter and reference electrodes were deposited on the opposite side of the pellet from a gold paste (Metalor A1644) annealed at 800 °C under air for 2 h. The catalytic activity measurements for the DOM were carried out at atmospheric pressure in a specific quartz reactor described elsewhere [23]. The reactive mixture composed of 2% of methane (Air Liquide, 5% ± 1,000 ppm CH_4 in He) and 10% of O_2 (Air Liquide, 99.95%) was controlled by flowmeters (Brooks). The overall flow rate was 10 L h^{-1} and helium was used as the carrier gas. The reactants and products were analyzed after condensation of water in a steam cooler (M&C Products, ECP1000-G) by on-line micro chromatograph (Varian CP2003) equipped with a Poraplot U column heated at 60 °C and a molecular sieve heated at 90 °C preceded by a back flush column. The catalytic behaviour of the electrochemical catalysts was compared with that of a reference catalyst (Pd-ref). The composition of this latter was optimized and contained nanoparticles of Pd (2.2 wt.%) dispersed on a gamma alumina support and doped with La_2O_3 (4 wt.%). Lanthanum stabilized alumina obtained from Grace was dry impregnated with a $Pd(NO_3)_2$ solution (8.3 wt.% Pd). The impregnated powder was then dried overnight at 150 °C and calcined at 600 °C for 2 h in air. A slurry was prepared with the impregnated powder (85%) and boehmite (15%), and milled in a Fritsch vibratory mill. An airbrush was used to deposit the required amount of slurry (corresponding to 5 mg dry powder) on the YSZ disc. The disc was then dried and calcined at 600 °C in air. The Pd dispersion was about 36%. This powdered reference catalyst was deposited on a YSZ pellet to be tested under similar operating conditions than those used for the electrochemical catalysts. The open circuit catalytic activity measurements under reactive mixture were recorded by heating the catalyst at 1 °C min^{-1} from 150 °C up to 750 °C. Before each catalytic activity measurement, the sample was pretreated under oxygen at 300 °C for 1 h and then cooled down to 150 °C under oxygen with a cooling rate of 1 °C min^{-1}. The reactive mixture was then introduced into the reactor. The conversion of methane was defined as the percentage of methane feed converted into CO_2, i.e.:

$$\mathrm{CH_4\ conversion}\ (\%)\ = \frac{P_{\mathrm{CH_4}_{\mathrm{inletgas}}} - P_{\mathrm{CH_4}_{\mathrm{outletgas}}}}{P_{\mathrm{CH_4}_{\mathrm{inletgas}}}} \times 100 \tag{3}$$

where P_{CH_4} inlet gas and outlet gas are the partial pressure of methane in the inlet and outlet gas, respectively. Carbon dioxide was the only oxidation product detected. The part of homogeneous reaction and also the rate of methane oxidation on the solid electrolyte and Au electrodes and wires were investigated and were found to be negligible (inferior to 1%) at temperatures below 700 °C.

3 Results and discussion

3.1 Catalytic activity measurements

3.1.1 Catalytic activity measurements under open-circuit

Table 1 summarizes the characteristics of the different samples tested and their catalytic behaviour at 350 °C for methane deep oxidation. The catalyst thickness varied from 11 to 75 nm (Table 1). The as-prepared films were quite dense. The Pd weight was estimated from the bulk density of Pd considering dense films. The Pd loading of the different samples is also indicated in Table 1 and ranges from 24 to 160 µg. The catalytic activities under open circuit of the Pd/YSZ electrochemical catalysts are presented in Fig. 1. For the samples prepared by PVD, the reaction rate at a given temperature was found to increase as the thickness of the Pd layer decrease except for the Pd1 sample. One can assume that this last had a so thin Pd layer that it did not cover the entire surface of the pellet. Billard and Vernoux [24] already reported that low thickness Pt catalysts did not cover all the YSZ support. Therefore, the catalytic activity was very low. The most effective electrochemical catalyst Pd2 exhibited a very thin layer of Pd in the order of 20 nm. This Pd2 sample might present a good dispersion as it turned out to exhibit a catalytic rate of 0.12 mmol s^{-1} g^{-1} at 350 °C, as reported in Table 1. However this value is inferior to 0.8 mmol s^{-1} g^{-1} (Table 1) measured at 350 °C for Pd-ref as it exhibited the highest reaction rate in this study. This value is close to the reaction rate reported by Epling and Hoflund [25] for a powder of Pd nanoparticles supported on alumina. Furthermore, methane was converted from 280 °C on Pd-ref whereas for the best sputtered catalyst, the conversion began from 340 °C. Finally, we can assume that the catalytic activity of the sputtered catalysts depends on both the pellet coverage by the film and the accessible metallic fraction. The most suitable film morphology might correspond to a monolayer of Pd atoms which would completely cover the YSZ pellet. Increasing the amount of Pd, as in the case of Pd3 and Pd4, did not enhance the activity by decreasing the Pd dispersion. The activation energies were calculated at low conversions in the temperature range

Table 1 Characteristics of the different samples and catalytic rates at 350 °C under open circuit conditions and at 500 °C under open circuit conditions for the Pd-ref and under +1 V for the sputtered electrochemical catalysts

Catalyst	Deposition duration (s)	Thickness (nm)	Pd loading (μg)	Catalytic rate at 350 °C (mmol CH_4 s^{-1} g^{-1} Pd)	Catalytic rate at 500 °C (mmol CH_4 s^{-1} g^{-1} Pd)
Pd1	15	11	24	0.11	2.1/+1 V
Pd2	30	24	58	0.12	5.6/+1 V
Pd3	60	52	110	0.03	1.1/+1 V
Pd4	90	75	160	0.04	1/+1 V
Pd-ref	–	–	110	0.8	8/OCV

Reactive mixture: CH_4/O_2: 2%/10%

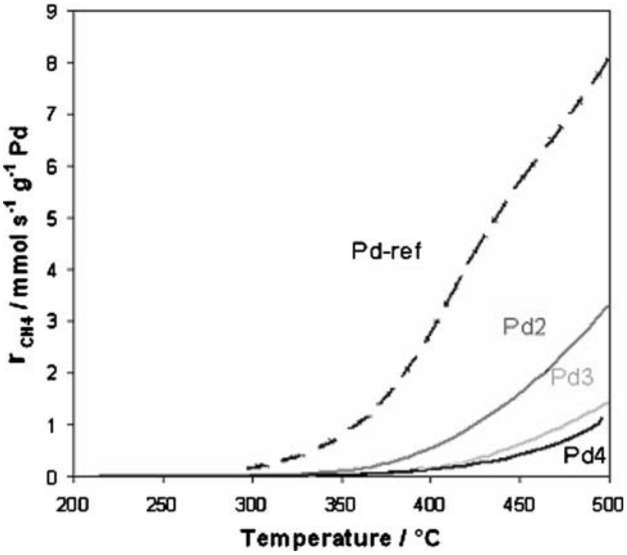


Fig. 1 Catalytic rate of methane versus temperature for different samples. Reactive mixture: CH_4/O_2: 2%/10%. Total flowrate: 10 L h^{-1}

between 300 and 400 °C using a linear regression on the Arrhenius plot by plotting ln *r* values as a function of the reverse of the temperature. The activation energy of Pd-ref was found to be 87 kJ mol^{-1}. Maillet et al. [26] calculated from temperature-programmed oxidation of methane on Pd/Al_2O_3 powders activation energies of 96 kJ mol^{-1} for the preoxidized sample and of 109 kJ mol^{-1} for the prereduced one. These values are in good agreement with those reported in this study. Hence the Pd-ref catalyst exhibited the same catalytic behaviour as that of powder catalysts. The activation energies of the three electrochemical catalysts were found to be quite similar to that of the Pd-ref, with 110 kJ mol^{-1} for Pd2, and 119 kJ mol^{-1} for Pd3 and 105 kJ mol^{-1} for Pd4.

3.1.2 *Catalytic activity measurement under closed-circuit*

The catalytic activity measurements under closed circuit showed that the activity of Pd/YSZ electrochemical catalysts can be strongly electropromoted in a reversible and controllable manner by the application of low currents or potentials. Only the effects of anodic polarizations are reported in this study corresponding to the migration of $O^{\delta-}$ from YSZ to the Pd surface. An example of EPOC experiment is presented in Fig. 2 for the sample Pd1 at 500 °C. During the first 14 h, the catalyst is under open circuit conditions. A strong deactivation of the catalyst was observed. This behaviour was ascribed to the Pd particles sintering currently observed on sputtered films as discussed in more detail in Sect. 3.1.3. Pd1 was kept at OCV for 14 h in order to stabilize the catalytic activity under reactive mixture before recording NEMCA experiments. Indeed, the deactivation of the performance during the first hours under reactive mixture was extremely fast. These conditions are not compatible with the investigation of the impact of the polarization on the catalytic activity. On the other hand, after 14 h, the deactivation is slower and NEMCA experiments can be performed. Then a current of +100 μA was applied to the catalyst leading to a sharp increase in the conversion of methane from 0.8 to 2.1%

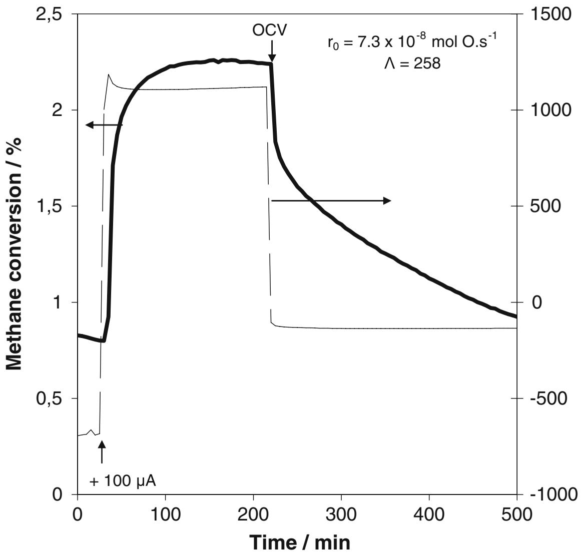


Fig. 2 Effect of a potential of +1 V at 500 °C on the methane conversion for the 10 nm-thick Pd1 sample. Reactive mixture: CH_4/O_2: 2%/10%. Total flowrate: 10 L h^{-1}

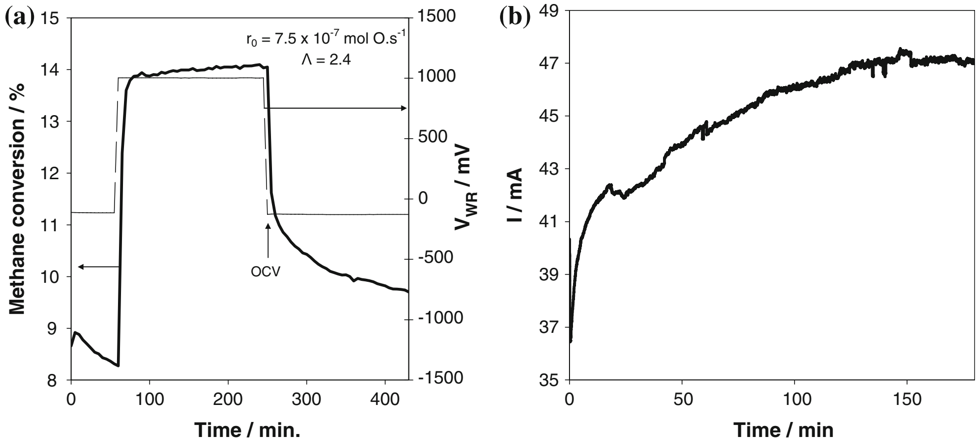


Fig. 3 Effect of a potential of +1 V at 500 °C on the methane conversion for the 24 nm-thick Pd2 sample. Reactive mixture: CH_4/O_2: 2%/10%. (**b**) Current curve corresponding to the applied polarization of +1 V of (**a**). Total flowrate: 10 L h^{-1}

(183% of conversion gain). The conversion rapidly reached a steady-state. The value of the faradaic efficiency was found to be 258 for an applied polarization of +100 μA (+1 V) demonstrating the ability of these catalysts to be electropromoted. This was the highest faradaic efficiency measured in this study for an anodic polarization. This behaviour under anodic polarization was observed for all the electrochemical catalysts as shown in Figs. 2–5. The electropromoted Pd2 sample showed a stable activity of 5.6 mmol of CH_4 per second and per gram of Pd at 500 °C (under +1 V) as reported in Table 1 similar to that of Pd-ref (8 mmol s^{-1} g^{-1}) under open circuit conditions at the same temperature. This electropromoted value was the highest reached in this study for the sputtered electrochemical catalysts. The electropromoted rates of Pd1, Pd3 and Pd4 were lower as summarized in Table 1. As the activity of Pd2 was stable under polarization (Fig. 3a), it can be assumed that the polarization slowed down or compensated the deactivation effect. The promotion might therefore be underestimated. The value of the faradaic efficiency was 2.4 under +1 V. The corresponding current is presented in Fig. 3b. The current gradually increased from 36 to 47 mA during the polarization. The given faradaic efficiency was calculated for an average current of 41 mA. This high value of the current explained the quite low faradaic efficiency. When the anodic polarization stopped, the methane conversion slowly decreased down to its initial value. This gradual decrease is due to a slow consumption of promoting $O^{\delta-}$ species by methane. The decay time, i.e. the time of consumption of oxygen, was 29 min for Pd2. This result seems to indicate that continuous polarization is not necessary to maintain an electropromoted state since the lifetime of promoting ionic species is quite high (several hours). This phenomenon was also observed on Pd1 (Fig. 2a), Pd3 (Fig. 4a) and Pd4 (Fig. 5a). The faradaic efficiency was still 7 for Pd2 about 3 h after the polarization had stopped. The thermal diffusion of $O^{\delta-}$ from YSZ to the surface of the catalyst at 500 °C could also contribute to maintaining this electropromoted state. The increase of the methane conversion under anodic polarization was also observed for Pd3 (Fig. 4a) and Pd4 (Fig. 5a) at 500 °C. For Pd3, the conversion increased from 4.8% to 6.5% under +1 V. The current increased slowly from 400 μA to 1.1 mA as shown in Fig. 4b during the 5 h of polarization. The faradaic efficiency was found to be 21 considering the maximum current value. The methane conversion was also enhanced by 50% under +1 V for Pd4 corresponding to a current of about 890 μA and a faradaic efficiency of 48. The evolution of the current during the polarization is presented in Fig. 5b. After 10 min polarization the current was almost stable. For both Pd3 and Pd4 catalysts, the conversion enhancement was sharp whereas the decrease, after the polarization was stopped, was gradual as already described for Pd1 and Pd2. The thickness of the Pd films modified the electrochemical properties. Hence, we assume that for low Pd thicknesses (Pd1), the coating did not cover the overall surface of the YSZ, and some particles could have been electrically isolated. The current was therefore low compared to Pd2 which exhibited the best electrochemical performances. Increasing the amount of Pd deposited on YSZ (Pd3 and Pd4), might not increase the number of three phase boundaries. Owing to the catalytic properties, Pd2 is expected to have the most suitable microstructure.

The increase in reaction rate of methane on Pd/YSZ under anodic polarization was already observed by Giannikos et al. [17] using Pd paint. They reported typical lambda values of 100 in the temperature range 350–450 °C, in good agreement with the results of this study. However, these electrochemical catalysts contained higher Pd loading with lower dispersions.

NEMCA experiments were also recorded at 600 °C on Pd3 and, as shown in Fig. 3, the activity was also found to be electropromoted by an anodic polarization. The methane conversion increased from 12 to 18% under +1 V and the value of the faradaic efficiency was 19. The current upon

Fig. 4 Effect of a potential of +1 V at 500 °C on the methane conversion for the 52 nm-thick Pd3 sample. Reactive mixture: CH_4/O_2: 2%/10%. (**b**) Current curve corresponding to the applied polarization of +1 V of (**a**). Total flowrate: 10 L h^{-1}

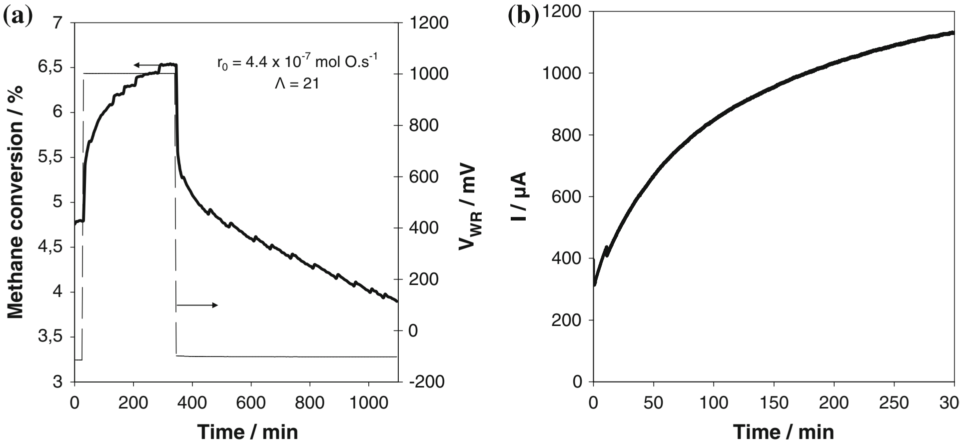


Fig. 5 Effect of a potential of +1 V at 500 °C on the methane conversion for the 75 nm-thick Pd4 sample. Reactive mixture: CH_4/O_2: 2%/10%. (**b**) Current curve corresponding to the applied polarization of +1 V of (**a**). Total flowrate: 10 L h^{-1}

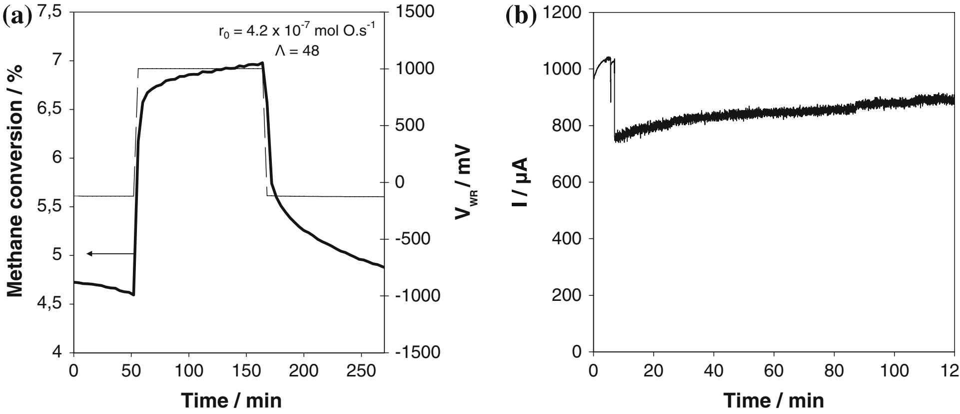
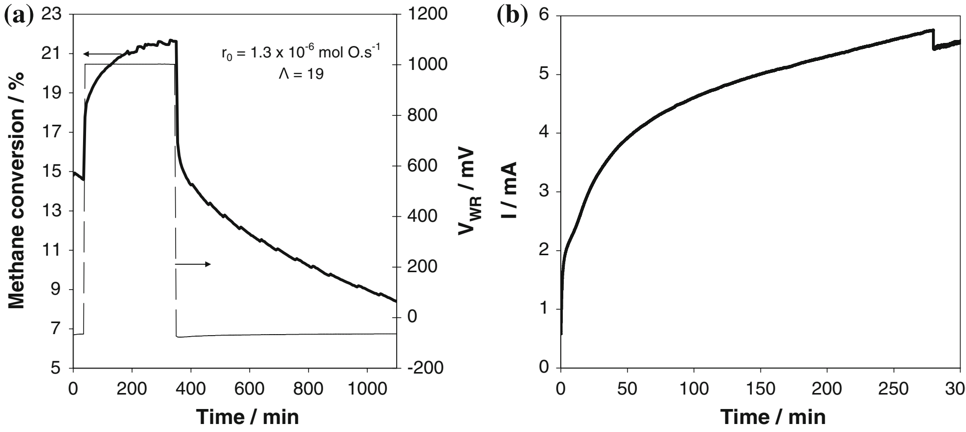


Fig. 6 (**a**) Effect of a potential of +1 V at 600 °C on the methane conversion for Pd3. Reactive mixture: CH_4/O_2: 2%/10%. (**b**) Current curve corresponding to the applied polarization of +1 V of (**a**). Total flowrate: 10 L h^{-1}



the application of +1 V is presented in Fig. 6b. It increased gradually to reach a maximum value of 5.8 mA, considered to calculate the faradaic efficiency. Therefore, it was possible to observe a NEMCA effect at a temperature as high as 600 °C despite the decrease in lifetime of the promoting species at the catalyst surface. No deactivation was observed under polarization as for the Pd2 sample. The conversion slowly returned to its initial value upon current interruption. According to the theory supported by Vayenas et al. [4], the presence of ionic promoters at the surface of a catalyst is at the origin of the modification of its adsorption properties. The faradaic efficiency can then be expressed as the ratio of the lifetime of the promoter at the surface of the catalyst to that of the adsorbed gaseous oxygen [4]. As the temperature increases, the lifetime of the promoter decreases as it desorbs to the gas phase or reacts at the three phase boundary. Therefore coverage and the faradaic efficiency decrease. Consequently, it should be more difficult to get a pronounced NEMCA effect at high operating temperatures. Vayenas et al. [4] clearly explained that the presence of promoters and the stability of the effective double layer at the metal/gas interface was of considerable importance to observe a NEMCA effect. Temperature Programmed Desorption (TPD) experiments could be performed to demonstrate the influence of temperature on the coverage of the promoter. As reported on Pt/YSZ [27], TPD spectra showed a desorption peak attributable to the ionic promoters centred at 640 °C and ending at 700 °C. In this system, it can be suggested that no NEMCA effect can be observed at temperatures higher than 700 °C. The maximum temperature on Pd/YSZ seems to be higher than on Pt/YSZ, as we observed a modification of the transition temperature of PdO to metallic palladium at a temperature as high as 700 °C (as discussed in Sect. 3.2). The promoters should still be present on the catalyst at those high temperatures.

In a previous study by Frantzis et al. [13] AC impedance spectroscopy was used to confirm the creation of an effective double layer at the Pd/gas interface due to the presence of the promoter oxygen ions. The authors ascribed the rate enhancement under anodic polarization to a modification of the work function of the catalyst under the action of the back-spillover of species from the electrolyte to the surface of the catalyst. Concerning the kinetic parameters, under a reducing environment [13] with an excess of methane or oxidizing reactive mixture [17], the kinetics were always found to be zero order with respect to oxygen partial pressure, indicating a high coverage of oxygen on the catalyst surface. In the present study the adsorption of methane is the rate limiting step. Therefore it can be suggested from previous work [3, 13, 17] that increasing the catalyst potential and work function decreases the binding strength of the adsorbed oxygen and therefore promotes its reaction with methane.

The rate enhancement ratio was found to increase with decreasing thickness of the palladium layer as shown in Fig. 7. This behaviour was already reported by Koutsodontis et al. [28] and was attributed to the decrease in amount of promoter on the gas exposed catalyst surface due to the reaction of $O^{\delta-}$ with the hydrocarbons in good agreement with a developed mathematical model.

3.1.3 *Sputtered electrochemical catalysts ageing*

The deactivation observed under reactive mixture for each electrochemical catalyst was studied in more detail on a fresh Pd4 sample. The catalyst was heated to 650 °C (temperature lower than that of the decomposition of palladium oxide as discussed in Sect. 3.1.3) at a heating and cooling rate of 1 °C min^{-1} and was maintained for 2 h at this temperature under 2% of CH_4 and 10% of O_2 with a total flow of 10 L h^{-1}. The subsequent cooling rate was also 1 °C min^{-1}. Two heating cycles were recorded. Figure 8 shows the methane conversion versus temperature between 350 and 650 °C. During the first heating cycle, the methane conversion gradually increased with temperature. During the plateau at 650 °C for 2 h, the activity sharply decreased from 53% to 43%. During the cooling, the activity was not recovered. The activity of the catalyst was found to decrease strongly between the two heating ramps. The temperature of 20% of methane conversion (T_{20}) was 481 °C for the first heating ramp, whereas it increased to 593 °C during the second heating. It can be suggested that the treatment at 650 °C for 2 h led to Pd particle sintering. This observation is in good agreement with the study of Jaccoud et al. [29] who reported the high sensitivity of sputtered electrodes to sintering. During the second plateau at 650 °C, the decrease in activity was clearly less pronounced and the activity at low conversion was almost entirely recovered when the temperature went down.

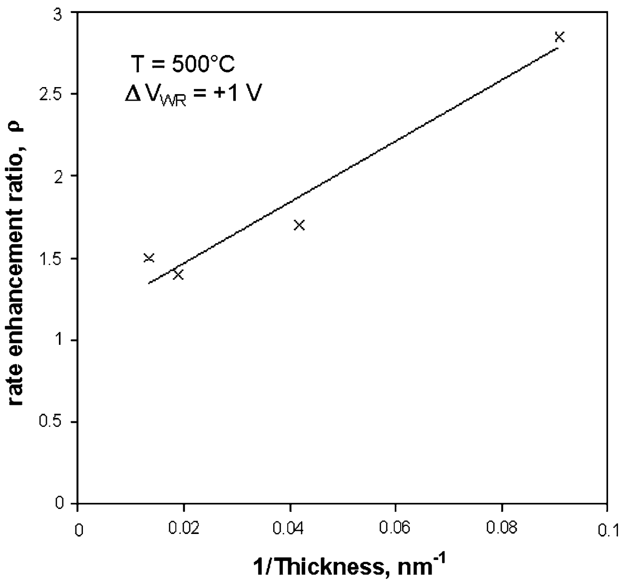


Fig. 7 Variation of the rate enhancement ratio with the reverse of the thickness of the catalyst layer at 500 °C for an applied potential of +1 V. Reactive mixture: CH_4/O_2: 2%/10%

3.2 Thermal treatments

All the samples were heated up to 750 °C with a heating and cooling rate of 1 °C min^{-1} under reactive mixture in order to analyze their thermal resistance associated with the PdO/Pd transition. The subsequent cooling rate was also 1 °C min^{-1}. DOM depends on the chemical state of the palladium [26]. The characteristic of the Pd-ref was first examined as a function of temperature (Fig. 9a). Methane conversion began at about 300 °C and increased rapidly with temperature. At 570 °C, the activity curve exhibited a

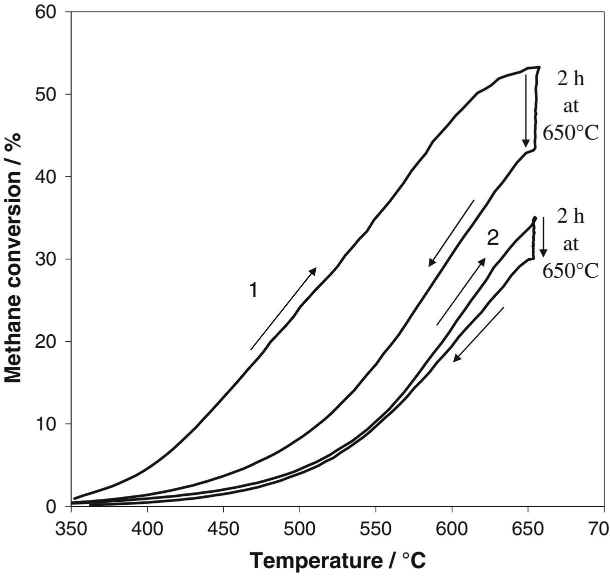
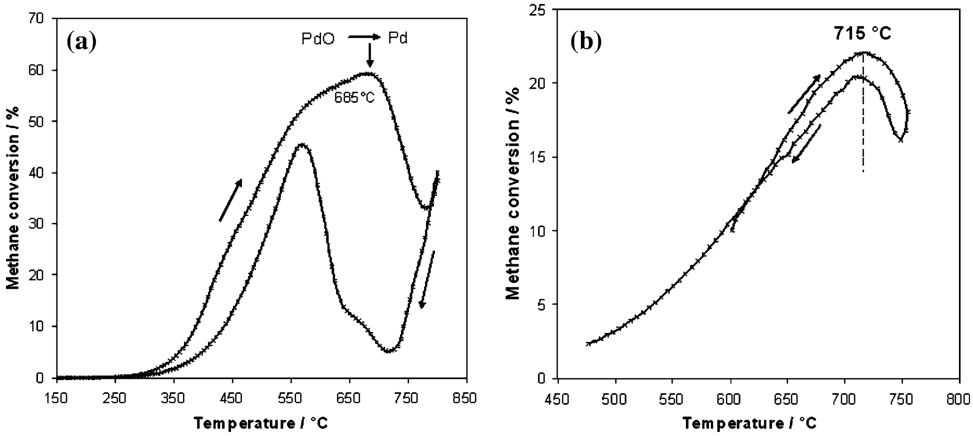


Fig. 8 Effect of heating cycles under reactive mixture CH_4/O_2: 2%/10% for the fresh Pd4 sample. Total flowrate: 10 L h^{-1}. Heating and cooling rates 1 °C min^{-1}

shoulder and was found to decrease sharply when the temperature exceeded 685 °C. This temperature should be the transition temperature of the transformation of PdO into metallic Pd. This value is close to that reported by Furuya et al. [30] who measured, by thermogravimetric analysis on a powder catalyst composed of Pd nanoparticles supported on YSZ a transition temperature of 700 °C under oxidizing reactive mixture (CH_4/O_2: 0.5%/5%). Indeed, the methane conversion dropped from 59% to 33% when the temperature increased from 690 to 775 °C. During cooling, methane conversion increased from 715 °C because formation of PdO occurred. A maximum of 45% was achieved at 575 °C. However, the activity was not recovered and strong deactivation was observed, attributable to particle sintering which explains the hysteresis. It is well-known that the transformation of PdO into metallic palladium leads to a decrease in activity partially due to irreversible sintering of Pd particles [26].

The electrochemical catalysts deposited by PVD were also heated to 750 °C but under an anodic polarization of +1 V in order to observe the effect of applied potential on the transition temperature. In the case of Pd3, the methane conversion increased with temperature up to 715 °C. Then a sharp drop in activity was observed from 22% to 16% of methane conversion when the temperature rose from 715 to 750 °C. The palladium oxide decomposition temperature was then 715 °C. This temperature was about 30 °C higher than that of Pd-ref without polarization. Moreover the observed deactivation was clearly less pronounced (Fig. 9b). This seems to indicate that the polarization, i.e. spillover of $O^{\delta-}$ species onto the Pd surface, could shift to higher PdO/Pd transition temperatures, then increasing the thermal resistance of the electrochemical catalyst. Su et al. [31] reported that the reduction of the oxide by methane proceeded by nucleation, small particles of metallic Pd being formed at the metal gas interface and further reduction occurring at the metal/oxide interface. This might be what happened under a reactive mixture without polarization. Jaccoud et al. [32] studied the "permanent" or "persistent" NEMCA effect observed on Pt/YSZ under anodic polarization when the temperature exceeds 400 °C. Under long-term positive polarization, a "persistent" NEMCA effect may be due to the formation of a layer of PtO_x at the catalyst/electrolyte interface. After current interruption, the persistence of the electropromoted state may be linked to gradual reduction of this PtO_x layer, leading to the formation of $O^{\delta-}$ promoting species that can spillover to the Pt surface. In the present case it can be suggested that palladium oxide might also be created under anodic polarization at the Pd/YSZ interface as our experiments also correspond to long-term anodic polarization. This may explain the conservation of the palladium oxide at higher temperatures than under open circuit conditions as long as polarization is applied and oxide ions are supplied to the catalyst. This assumption is in good

Fig. 9 (**a**) Methane conversion versus temperature for the Pd-ref catalyst at OCV. (**b**) Methane conversion versus temperature for the Pd3 catalyst under +1 V. Reactive mixture: CH_4/O_2: 2%/10%. Total flowrate: 10 L h^{-1}. Heating and cooling rates 1 °C min^{-1}



agreement with transient experiments (Figs. 2, 3) where, in spite of high temperatures (500 and 600 °C), the methane conversion fell very slowly to its initial value after current interruption, suggesting a "persistent" NEMCA effect, due to PdO layer formation.

4 Conclusions

The catalytic activity of electrochemical Pd/YSZ with layers of Pd deposited by PVD can be in situ controlled under polarization for the DOM. Rate enhancements exceeding the ionic current were observed with high faradaic efficiencies (NEMCA effect) under anodic polarization. Therefore PVD appears to be a suitable technique for the preparation of thin electrodes. The catalytic activity per gram of catalyst of an electropromoted film with the most suitable microstructure was found to be similar to that of a reference optimized catalyst. Experiments indicated a significant deactivation of the sputtered catalysts below the transition temperature due to particle sintering. Polarization increased the transition temperature of PdO/Pd by 30 °C and the deactivation was clearly less pronounced than without polarization. The applied potential enhanced the thermal stability of the catalyst, which is of industrial interest in order to increase the catalyst lifetime and enlarge the operating temperature window.

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