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Electrochemical Promotion of Propane and Methane Oxidation on Sputtered Pd Catalyst-Electrodes Deposited on YSZ

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Abstract The microstructure and electrochemical promotion of thin Pd catalyst-electrodes deposited on yttria-stabilized zirconia and prepared by sputter-deposition has been studied for the complete oxidation of propane and methane using steady state catalytic measurements in conjunction to electrochemical studies under lean conditions and at temperatures from 320 to 450 °C. It was found that propane oxidation is favoured on the metallic Pd film, while methane oxidation is enhanced after partial oxidation of the sputtered film in the course of the experiments. The observed rate changes under anodic polarization were strongly non-Faradaic and exceeded the electrocatalytic rate, *I*/2*F*, of O^{2-} supply to the catalyst by up to a factor of 150 for methane and 250 for propane combustion. The catalytic rate increases only moderately by up to a factor of 2 and 3, respectively. For both reactions the catalyst-electrodes exhibit electrophobic behaviour, i.e. the rate increases with anodic polarization and decreases slightly with cathodic polarization.

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1 Introduction

Palladium is an important and unique catalyst for the deep oxidation of hydrocarbons such as methane [1–5] and propane [6–8]. Since Pd is expensive and its availability is limited, the reduction of the amount of catalyst and the better promotion of its catalytic properties is of great importance. The combustion of light hydrocarbons in an electrochemical membrane reactor [9–11], in which the catalyst, e.g. Pd is deposited on an oxygen ion conducting support, is a challenging alternative to their conventional catalytic combustion, especially under conditions of electrochemical promotion.

Electrochemical promotion of catalysis (EPOC), or non-Faradaic electrochemical modification of catalytic activity (NEMCA) is a well established electrochemical concept which allows for in situ and reversible tuning of catalytic performance by applying externally a potential or current between the catalyst-working and the counter electrode, as shown in Fig. 1 [12–15]. Catalyst and counter-electrode are deposited on the solid electrolyte, i.e. yttria-stabilized zirconia (YSZ). Upon application of positive current or potential, O^{2-} species are supplied from the YSZ to the catalyst surface at a rate *I*/2*F*. The electrochemically generated O^{2-} species migrate (back-spillover) over the entire gas-exposed catalyst-electrode surface and cause changes in its electronic properties, which are accompanied by alterations in the chemisorptive and catalytic properties of the catalyst-electrode. The effect of potential or current on the catalytic activity is usually described by two parameters, i.e. the rate enhancement ratio, ρ, defined as

$$\rho = r/r_o \qquad (1)$$

where r_o is the catalytic rate at open circuit and r, the catalytic rate under polarization, and the apparent Faradaic efficiency, Λ, defined as

$$\Lambda = (r - r_o)/(I/2F) \qquad (2)$$

where I is the applied current, F is the Faraday constant, and $I/2F$ equals the rate of O^{2-} supply to the catalyst [12–15].

The deep oxidation of light hydrocarbons has been studied extensively for methane oxidation on Pt [16], Pd [17–24] and Rh [25, 26] as well as for propane combustion on Pt [27–34] and Rh [35]. Methane combustion on organometallic Pd paste electrodes deposited on YSZ can by electrochemically promoted under slightly reducing reaction conditions, as shown by Bebelis et al. and co-workers [17, 18], with a final rate increase of up to $\rho = 70$ or 90 under anodic polarization. On sputter-deposited [19, 20] and impregnated Pd/YSZ samples [21] methane oxidation has been carried out only in excess of oxygen. The observed rate enhancement ratio, ρ, is in both cases small and ρ values of up to 2–3 have been reached at high temperatures of 470–600 °C [19–21]. In most recent studies [22–24], sputter-deposited and impregnated Pd films have been pretreated in a reactive C_2H_4/O_2 mixture to allow for low temperature ignition of the electrochemically promoted methane oxidation. XRD and XPS studies in conjunction with electrochemical investigations show, that the as-prepared sputtered catalyst-electrodes (which consist mainly of a Pd metal phase), are able to electrochemically promote CH_4 oxidation, while impregnated films (which mainly consist of a PdO phase) can be electropromoted only after in situ reduction [24]. This led to the conclusion that the PdO phase is necessary for significant catalytic activity towards methane combustion, but the Pd metal phase is required for successful electrochemical promotion.

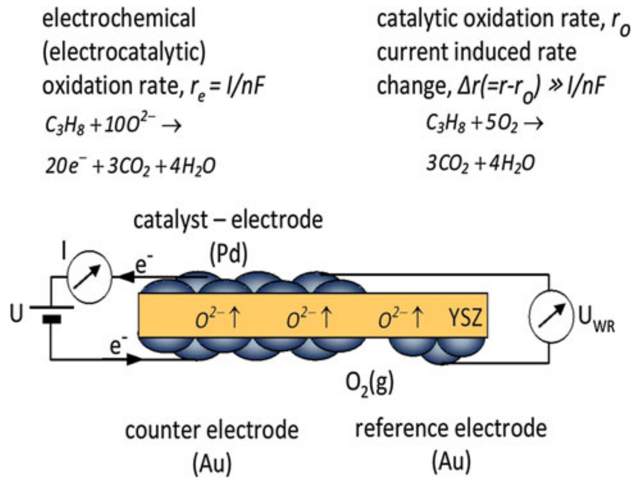


Fig. 1 Principle and basic experimental setup for electrochemical promotion (NEMCA) studies, here for the case of propane oxidation, using an O^{2-} conducting solid electrolyte (YSZ)

The present work has focused on Pd sputter-deposited catalyst-electrodes on YSZ to achieve uniformly thin film deposition with low Pd loadings. The work was carried out only under excess of oxygen and low temperatures (350 °C) in order to replicate technology demands of emission and pollution control. Methane and propane combustion are compared in terms of their catalytic activity under open and closed circuit conditions, and also in terms of their reaction kinetics in order to relate the influence of the Pd^0/PdO redox couple with the ability to electrochemically promote both catalytic oxidations. Furthermore, attention has been paid to the catalyst-electrode morphology and its possible modification during catalytic and electrocatalytic experiments.

2 Experimental

The solid electrolyte was a pellet of 8 mol% Y_2O_3-stabilized ZrO_2 (YSZ) of 18 mm diameter and 2 mm thickness provided by Ceraflex. Prior to Pd or Au deposition, no surface treatment was performed. Inert gold counter and reference electrodes were deposited on one side of the support before the Pd catalyst-electrode was applied. Gold organometallic paste (Metalor, A1118) was used for the deposition of the counter and reference electrodes in the case of methane oxidation. The Au films were calcined in air at 650 °C for 1 h. Gold sputter deposition was used for the preparation of the counter and reference electrodes in the case of propane oxidation. A pure Au (99.95 %) target provided by MatecK GmbH was used. Substrate temperature was kept at 50 °C and the sputtering chamber was filled with pure argon. The sputtering conditions were the following: direct current (dc) mode with a discharge of 455 V. Blank experiments have shown that paste- and sputtered-deposited gold films are catalytically inactive for both propane and methane oxidation [12, 13].

The Pd film (catalyst-electrode) was deposited on the other side of the solid electrolyte. A pure Pd (99.95) target provided by MatecK GmbH was used. The sputtering conditions were the following: dc mode with a discharge of 376 V. Substrate temperature was kept at 50 °C and the sputtering chamber and filled with pure argon. During sputter-deposition the substrates were placed 55 cm far from the target which was found to result in good uniformity of the produced Au and Pd films. The final Pd loading was measured by weighting the samples and was 0.8 ± 0.1 mg Pd for all samples. The geometric surface area of the sputtered Pd working electrode was 2 cm^2.

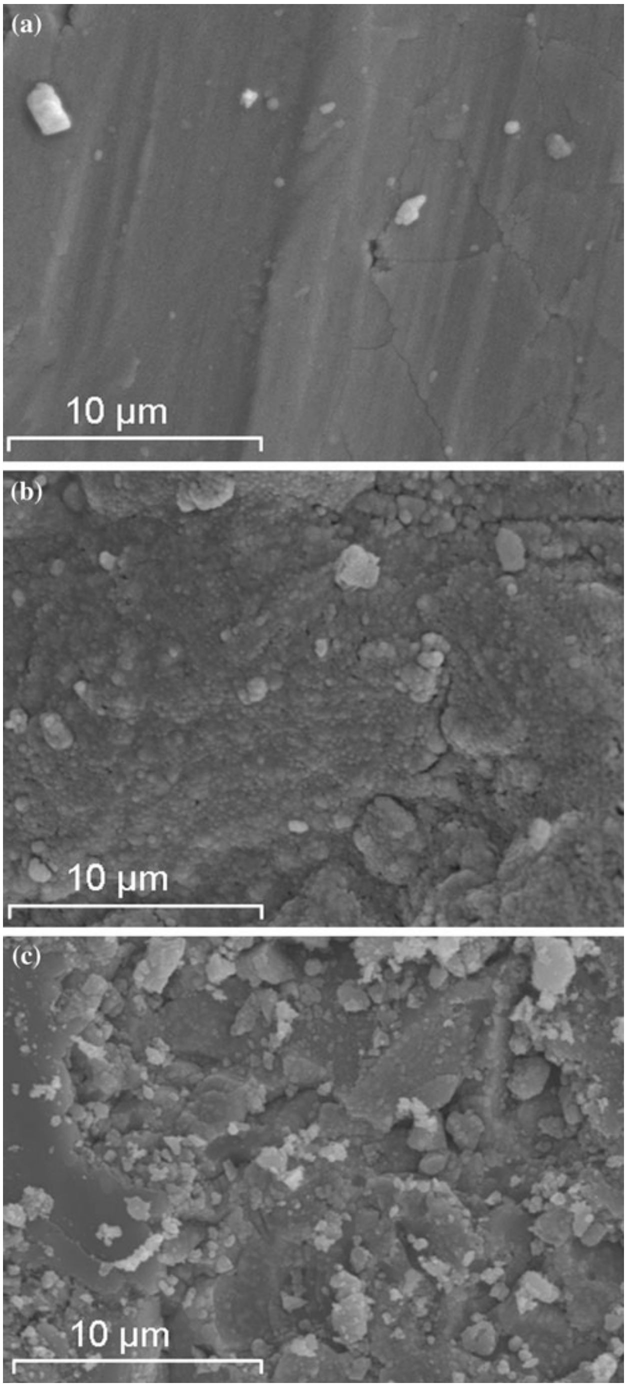


Fig. 2 SEM micrographs of **a** as prepared sputtered Pd/YSZ catalyst electrode, **b** Pd film after propane oxidation, **c** after methane oxidation

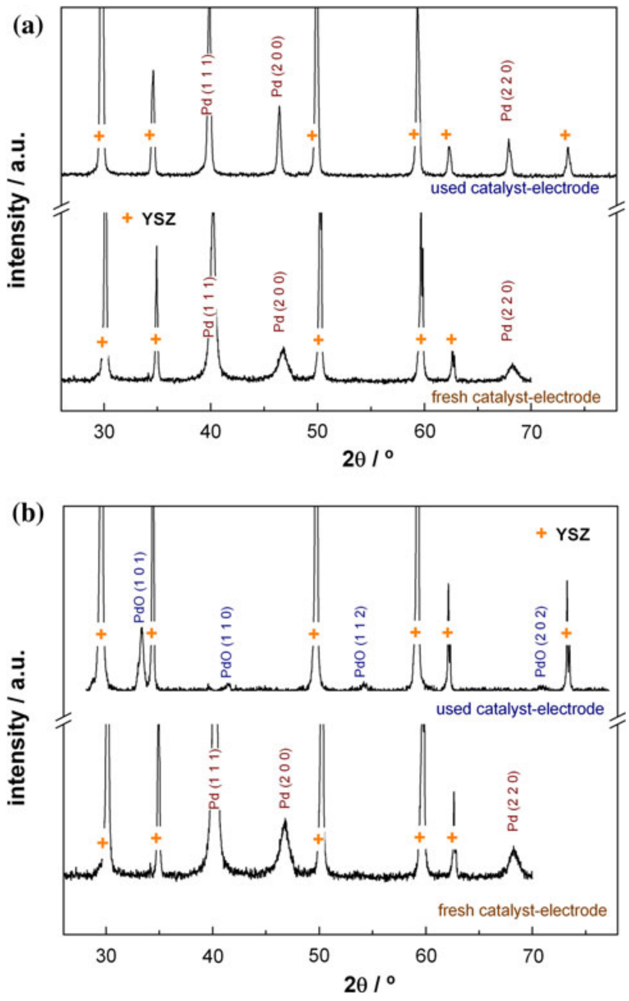


Fig. 3 XRD spectra for sputtered Pd/YSZ catalyst electrode before and after exposure to reaction conditions **a** propane oxidation, **b** methane oxidation

The catalytic and electrocatalytic experiments were carried in a quartz reactor in which all three electrodes are exposed to the same gas mixture under atmospheric pressure [12]. Reactant gases were composed of 3.5 % C_3H_8 in He (Linde), 5.6 % CH_4 in He (L'Air), 20 % O_2 in He (Linde) and He (L'Air Liquide, 99.995 % purity) as the carrier gas.

Gas analysis of the reactants and products was performed using on-line gas-chromatography (Shimadzu A14 with a thermal conductivity detector). The infrared analyzer Rosemount Binos 100 was used for continuous measurements of the CO_2 concentration signal.

Denoting by $y^o_{C_3H_8}$, $y_{C_3H_8}$ and y_{CO_2} the reactor inlet ($y^o_{C_3H_8}$) and outlet ($y_{C_3H_8}$,y_{CO_2}) C_3H_8 and CO_2 mol fractions, one computes the rate, r, of complete propane oxidation:

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \qquad (3)$$

expressed in mol O/s from:

$$r = (10/3)\ \mathrm{G} y_{CO_2} \qquad (4)$$

where G (mol/s) is the total molar flowrate through the reactor. Denoting by $y^o_{CH_4}$, y_{CH_4} and y_{CO_2} the reactor inlet ($y^o_{CH_4}$) and outlet (y_{CH_4}, y_{CO_2}) CH_4 and CO_2 mol fractions, one computes the rate, r, of complete methane oxidation:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (5)$$

expressed in mol O/s from:

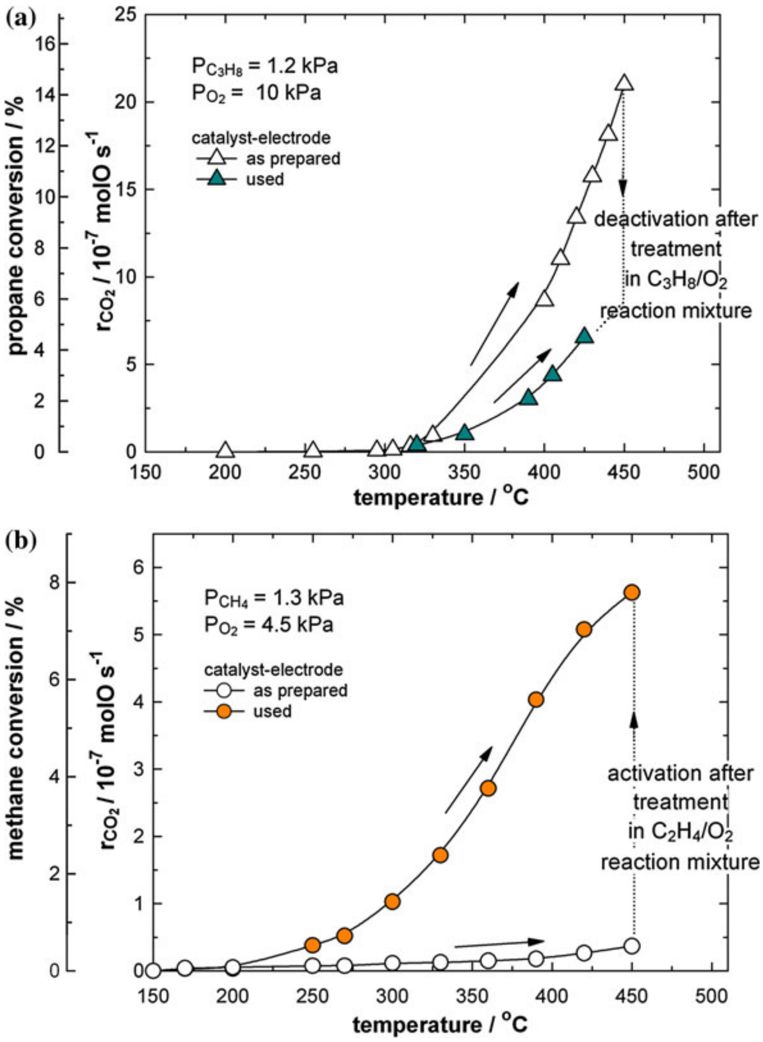


Fig. 4 Steady-state effect of temperature on **a** propane and **b** methane conversion and concomitant CO_2 formation rates as a function of temperature under open circuit conditions. *Open symbol* present the first light off prior treatment, *closed symbols* show results obtained with a used catalyst. Catalyst: thin sputtered Pd film deposited on YSZ. Feed composition:
(a) $P_{C_3H_8} = 1.2$ kPa, $P_{O_2} = 10$ kPa, $F_v = 170$ cm^3 min^{-1} (STP)
(b) $P_{CH_4} = 1.3$ kPa, $P_{O_2} = 4.5$ kPa, $F_v = 200$ cm^3 min^{-1}(STP)

$$r = 4\,Gy_{CO_2} \tag{6}$$

The propane and methane conversion to CO_2 are defined from:

$$C_3H_8\,conversion = [(y^o_{C_3H_8} - y_{C_3H_8})/y^o_{C_3H_8}] \cdot 100 \tag{7}$$

$$CH_4\,conversion = [(y^o_{CH_4} - y_{CH_4})/y^o_{CH_4}] \cdot 100 \tag{8}$$

The structure and morphology characterization of the different catalytic layers was carried out by scanning electron microscopy (SEM) using a JEOL JSM-6300 microscope.

The crystalline phases of the palladium catalysts and its YSZ support were examined by X-ray powder diffraction (XRD) performed in a PANalytical diffractometer equipped with a X'Celerator detector with monochromatic Cu Kα1 radiation ($\lambda = 1.54$ Å). XRD patterns were recorded in the 2θ range between 10° and 70°, with a scan step size of 0.02 °/s.

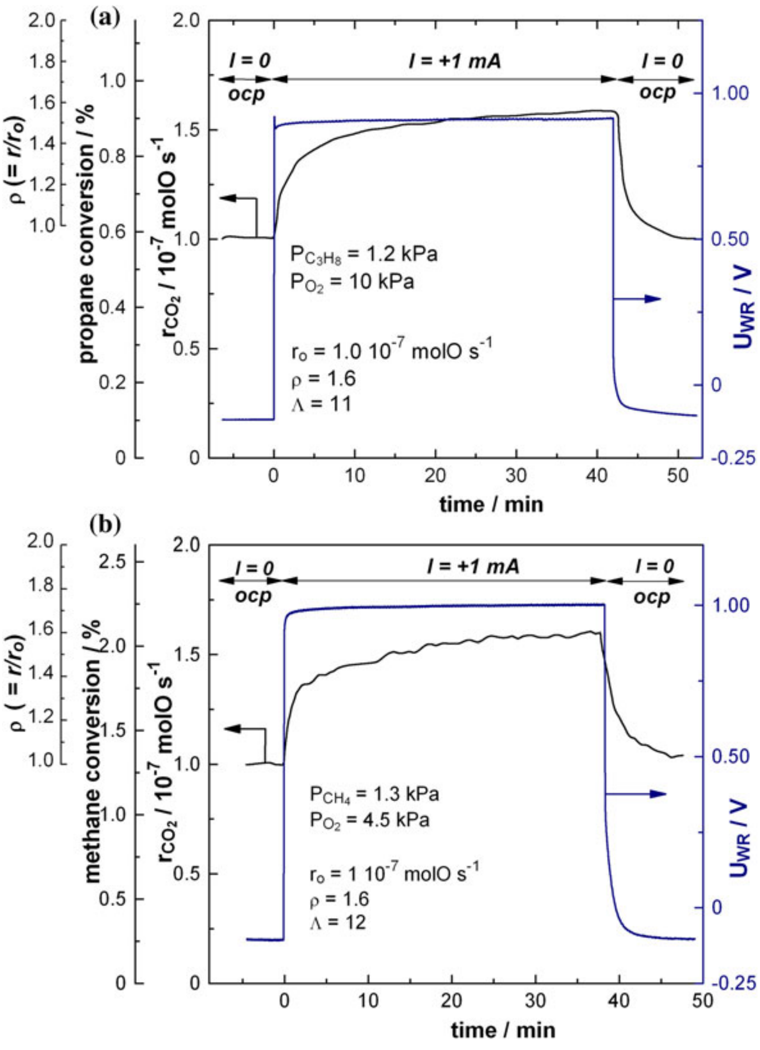
Currents or potentials were applied by means of a Solartron 1286 electrochemical interface.

3 Results and Discussion

3.1 Catalyst Characterization

The surface morphology of the catalyst was studied using SEM and XRD after preparation and after catalytic and electrocatalytic experiments. Figure 2a–c shows the main morphological features of the Pd film deposited on YSZ. The fresh prepared Pd film (Fig. 2a) exhibits a smooth surface and covers uniformly the YSZ support. The grains of the underlying YSZ support are to be seen, which confirms the uniformity and small thickness of the freshly sputtered film. The films are 2–5 µm thick, as estimated from cross section SEM photographs, and adhere very well on the solid electrolyte support. As expected, the Pd film was morphologically unstable during methane and propane oxidation. After propane combustion experiments the film is still smooth and shows clearly an improved crystallinity (Fig. 2b), while after methane oxidation the Pd particles exhibit irregular distribution in size (2–50 µm) and shape

Fig. 5 Rate, r_{CO2}, and catalyst potential, U_{WR}, response to a step change in applied positive current of 1 mA at T = 350 °C for **a** propane and **b** methane combustion. Catalyst: thin sputtered Pd film deposited on YSZ. Feed composition, as in Fig. 4



(Fig. 2c). The formation of cavities and voids is observed, which is most likely due to the formation of Pd oxide as discussed in the following paragraph.

The XRD patterns (Fig. 3) show different phases for the as-prepared and used catalysts. The crystal planes of the deposited films were identified according to the JCPDS crystallographic data base [36]. The solid electrolyte shows for all samples the characteristic peaks of YSZ, $Zr_{0.8}Y_{0.2}O_{1.9}$ corresponding, to the (111), (200), (220) and (311) planes (JCPDS-ICDD Card No. 01-082-1246 [36]). Fresh sputtered samples show peak reflections only for the metallic Pd phase (Fig. 3a, b), which is consistent with a face-centered cubic (fcc) structure where reflections appear at 40.1°, 46.6° and 68.1° corresponding to the (111), (200) and (220) planes of Pd^0 (JCPDS-ICDD Card No. 05-0681 [36]). The presence of only metallic Pd for the fresh sputtered sample is expected since the film has been produced with a high purity palladium sputtering target in Ar environment without further treatment. After propane oxidation (Fig. 3a) only peak reflections of metallic Pd are observed. After methane oxidation the Pd phase has been at least partially oxidized (Fig. 3b) since only peak reflections appearing at 33.8°, 41.9°, 54.7° and 71.3° are found, which correspond to the (101), (110), (112) and (202) planes of PdO (JCPDS-ICDD Card No. 41-1107 [36]). The metallic Pd phase is not detectable via XRD for the used catalyst films.

3.2 Catalytic Activity Measurements

Figure 4 shows the steady-state effect of temperature on (a) propane and (b) methane conversion and their concomitant CO_2 formation rates under open circuit conditions. The onset for propane combustion is found at 320 °C, while the onset of methane combustion is observed at temperatures around 250 °C. The first light off obtained with a mainly metallic Pd film leads to a propane conversion value of 12 % at 450 °C. The conversion decreases to only 4 % when the catalyst is exposed for 2 h to the reactive propane/oxygen reaction mixture at 450 °C. The

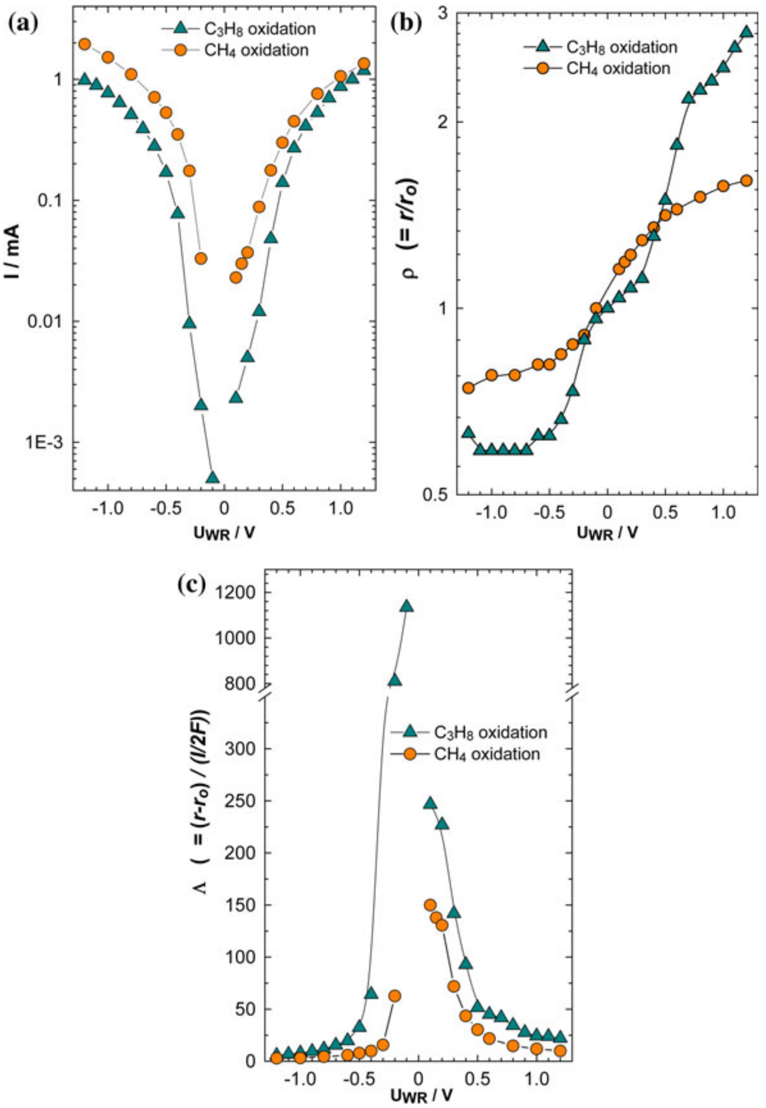


Fig. 6 Steady state effect of applied potential on the electrochemically promoted (*triangle*) propane and (*circle*) methane oxidation at 350 °C. **a** Tafel plots, **b** effect of applied potential on the rate enhancement ratio, ρ. **c** effect of applied potential on Faradaic efficiencies, Λ. Feed composition, as in Fig. 4

opposite behavior is observed for a sputtered Pd film in the course of methane oxidation where the conversion for the as prepared catalyst is smaller than 1 % at the highest temperature of 450 °C. The used catalyst, however, shows significant higher catalytic activity since it has been exposed to a reactive lean C_2H_4/O_2 gas mixture. The CH_4 conversion after this treatment increased to 8 % at 450 °C.

The results in Fig. 4a, b strongly suggest that PdO is indeed the more active phase for methane combustion while the metallic Pd phase is responsible for high propane conversion rate.

3.3 Electrochemical Promotion Experiments

Electrochemical promotion experiments have been carried out after propane or methane conversion has been stabilized, i.e. after the second light off experiment (Fig. 4). Figure 5a, b show the transient effect of a constant positive current application on the catalytic CO_2 formation rate and on the potential difference for (a) propane and (b) methane oxidation at 350 °C. A reversible rate enhancement is observed in both cases. The increase in the catalytic rate, Δr, is relatively small with ρ values of 1.6, but significantly higher than the rate of ion transport, $I/2F$. At the beginning of the experiment in Fig. 5a, at $t < 0$, an open circuit rate of 1×10^{-7} molO s^{-1} is observed while the catalyst potential is equal to -50 mV. At $t = 0$ a constant current of 1 mA is applied galvanostatically and O^{2-} ions are transferred to the Pd film at a rate $I/2F = 5.2 \times 10^{-9}$ molO s^{-1}. This induces an increase in the catalytic rate to a new value of 1.6×10^{-7} molO s^{-1}, i.e. the rate enhancement $\rho\ (= r/r_o)$ equals 1.6. The corresponding steady state value of the catalyst potential, U_{WR}, equals 900 mV. The rate increase $\Delta r\ (= r - r_o) = 0.6 \times 10^{-7}$ molO s^{-1} is 11 times larger than the rate of O^{2-} supply $I/2F$, i.e. the Faradaic efficiency, Λ, equals 11.

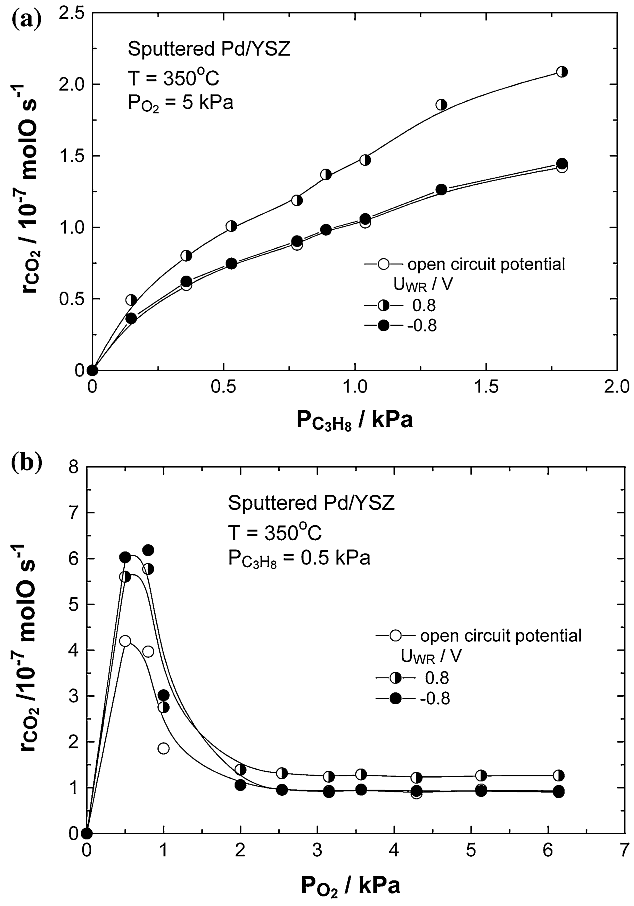


Fig. 7 Dependence of open and closed circuit rate of propane oxidation on **a** $P_{C_3H_8}$ at constant P_{O_2} ($P_{O_2} = 5$ kPa) and on **b** P_{O_2} at constant $P_{C_3H_8}$ ($P_{C_3H_8} = 0.5$ kPa) at 350 °C

In the case of methane oxidation the rate increase is similar with $\Delta r\ (= r - r_o) = 0.55 \times 10^{-7}$ molO s^{-1} which leads to an almost equal Faradaic efficiency, Λ, of 12.

Figure 6a shows, in the form of a Tafel plot, the current versus applied potential, U_{WR} dependence, for both reactions at 350 °C. The exchange current, I_0, is, in the case of methane oxidation, slightly higher for propane oxidation: 0.2 versus 0.08 mA. Figure 6b shows the steady state effect of the applied potential on the rate enhancement, ρ, for both oxidation reactions. Under overall oxidizing conditions, anodic polarization leads to an increase in catalytic rate and cathodic potential application leads to a decrease in rate. Figure 6c shows the effect of the applied potential on the Faradaic efficiency parameter, Λ, for the two combustion reactions. The enhancement factor, Λ, reaches value of up to 150 for methane and 250 for propane oxidation at low overpotentials. This number expresses the number of catalytic turnovers promoted by each electrochemically supplied O^{2-} before its ultimate consumption by the fuel. In agreement with previous studies on electrochemical promotion [12–14] the order of magnitude of the measured enhancement factors, Λ, is in good qualitative agreement with the parameter $2Fr_o/I_0$, which is found to be equal to 220 and 180, respectively.

According to the rules of electrochemical and classical promotion [12, 13] the observed electrophobic behavior suggests that the catalytic rate must be positive order in the fuel (methane or propane) and zero or negative order in oxygen. This is indeed the case for propane oxidation, as shown in Fig. 7, obtained after prolonged catalyst utilization, but also for methane oxidation (Figs. 4, 5 in Ref. [18]). At high oxygen partial pressures, as is the case in the present study, the oxygen coverage is high and the Pd active sites are occupied almost entirely by oxygen. Surface PdO is formed at the expense of surface Pd^0. This is apparently the reason why in excess of oxygen the electrochemical promotion effect is smaller than in the case of reducing conditions for the same reaction [18], since anodic polarization of the Pd film is apparently not sufficient to decompose, at least partially the surface PdO layer, as in the case of Rh films [37]. This is in line with recent work which has shown that CH_4 oxidation on Pd can be electropromoted under lean conditions only with sputtered and not with impregnated Pd films, since the latter consist primarily of PdO [24]. It is also consistent with the higher activity of partially reduced PdO observed in pulsed methane combustion experiments [38]. These results showed that catalyst activity initially increased with the degree of reduction, reaching a maximum and then decreasing continuously as the oxygen is depleted.

4 Conclusions

Sputter-deposited Pd films deposited on YSZ can be electrochemically promoted for methane and propane oxidation, even under oxidizing conditions in the temperature range 320–450 °C. The XRD results provide clear evidence for a Pd-PdO phase transformation only after methane oxidation, which shows partial oxidation of Pd in the course of the experiments. This phase transition appears to activate the catalyst for methane oxidation. This suggests that PdO is required for low temperature methane oxidation and metallic Pd for the ability of electropromotion. Open circuit propane oxidation is favored by the metallic Pd phase, and can be further increased via the application of a potential or current. Upon application of anodic potential, both the methane and propane oxidation rates are reversibly enhanced by up to a factor of 2 for methane, and up to 3 for propane oxidation, with Faradaic efficiencies of 150 and 250, respectively. The observed electrophobic electropromotion behavior is consistent with the rules of electropromotion.

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References

1. Ciuparu D, Lyubovsky MRL, Altman E, Pfefferle LD, Datye A (2002) Catal Rev 44:593
2. Forzatti P (2003) Catal Today 83:3
3. Gélin P, Primet M (2007) Appl Catal B 39:1
4. Centi G (2001) J Mol Catal A 173:287
5. Chin YH, Resasco DE (1999) Catalysis 14:1
6. Maillet T, Solleau C, Barbier J Jr, Duprez D (1997) Appl Catal B 14:85
7. Demoulin O, Le Clef B, Navez M, Ruiz P (2008) Appl Catal A 344:1
8. Glinrun T, Mekasuwandumrong O, Panpranot J, Chaisuk C, Praserthdam P (2010) React Kinet Mech Catal 100:441
9. Lai BK, Kerman K, Ramanathan S (2011) J Power Sour 196:6299
10. Liang F, Zhou W, Vhi B, Pu J, Jiang SP, Jian L (2011) Int J Hydrog Energy 36:2040
11. Ariful Hoque Md, Lee S, Park NK, Kim K (2012) Catal Today 185:66
12. Vayenas CG, Bebelis S, Pliangos C, Brosda S, Tsiplakidis D (2001) Electrochemical activation of catalysis: promotion electrochemical promotion and metal-support interactions. Kluwer/Plemum, New York
13. Vayenas CG, Koutsodontis CG (2008) J Chem Phys 128:182506
14. Foti G, Bolzonella I, Comninellis Ch (2003) In: Vayenas CG, Conway BE, White RE (eds) Modern aspects of electrochemistry, vol 36. Kluwer/Plenum, New York
15. Jiménez-Borja C, de Lucas-Consuegra A, Valverde JL, Dorado F, Caravaca A, Gonzáles J (2012) In: Taylor JC (ed) Advanes in chemical research, Chap 4, vol 14. Nova Science, New York. ISBN 978-1-61942-327-5
16. Tsiakaras P, Vayenas CG (1993) J Catal 140:53
17. Giannikos A, Frantzis AD, Pliangos C, Bebelis S, Vayenas CG (1998) Ionics 4:53
18. Frantzis AD, Bebelis S, Vayenas CG (2000) Solid State Ion 136/137:863
19. Roche V, Karoum R, Billard A, Revel R, Vernoux P (2008) J Appl Electrochem 38:1111
20. Roche V, Revel R, Vernoux P (2010) Catal Commun 11:1076
21. Jiménez-Borja C, Dorado F, de Lucas-Consuegra A, García-Vargas JM, Valverde JL (2009) Catal Today 146:326
22. Jiménez-Borja C, Brosda S, Makri M, Sapountzi F, Dorado F, Valverde JL, Vayenas CG (2012) Solid State Ion. doi:10.1016/j.ssi.2012.03.004
23. Jiménez-Borja C, Brosda S, Matei F, Makri M, Delgado B, Sapountzi F, Ciuparu D, Dorado F, Valverde JL, Vayenas CG (2012) Appl Catal B. doi:10.1016/j.apcatb.2012.02.011
24. Matei F, Ciuparu D, Jiménez-Borja C, Dorado F, Valverde JL, Brosda S (2012) Appl Catal B 127:18
25. Baranova EA, Fóti G, Comninellis Ch (2004) Electrochem Commun 6:170
26. Nakos A, Souentie S, Katsaounis A (2010) Appl Catal B 101:31
27. Butel L, Hénault M, Roux C, Siebert E, Béguin B, Gaillard F, Primet M, Vernoux P (2002) Ionics 8:136
28. Vernoux P, Gaillard F, Bultel L, Siebert E, Primet M (2002) J Catal 208:412
29. Bultel L, Roux C, Siebert E, Vernoux P, Gaillard F (2004) Solid State Ion 166:183
30. Bultel L, Vernoux P, Gaillard F, Roux C, Siebert E (2005) Solid State Ion 176:793
31. Souentie S, Lizarraga L, Papaioannou EI, Vayenas CG, Vernoux P (2010) Electrochem Commun 12:1133
32. Lizarraga L, Guth M, Billard A, Vernoux P (2010) Catal Today 157:61
33. Kokkofitis C, Karagiannakis G, Zisekas S, Stoukides M (2005) J Catal 234:476
34. Kokkofitis C, Stoukides M (2006) J Catal 243:428
35. Bebelis S, Kotsionoploulos N (2006) Solid State Ion 177:2205
36. JCPDS-ICD, PCPDFWIN, Version 2.2 June 2001
37. Baranova EA, Thursfield A, Brosda S, Foti G, Comninellis C, Vayenas CG (2005) J Electrochem Soc 152(2):E40
38. Ciuparu D, Pfefferle L (2001) Appl Catal A 218:197