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Complete oxidation of methane on Pd/YSZ and Pd/CeO_2/YSZ by electrochemical promotion

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ABSTRACT

In this work, methane combustion over Pd/YSZ and Pd/CeO_2/YSZ catalyst was investigated at a temperature range of 470–600 °C. For the first time, the feasibility of electrochemical promotion on palladium films prepared by wet impregnation was reported. The catalytic activity of palladium was found to increase over 160% via transference of oxygen ions from the solid electrolyte to the catalyst film. In addition, palladium supported over ceria and yttria-stabilized zirconia showed the highest activity. As expected, the presence of ceria allowed improving the oxygen storage capacity of the catalyst system.

1. Introduction

Catalytic oxidation is the most attractive choice to obtain thermal energy from methane. Natural gas is a major source of thermal energy with industrial interest due to its abundance, and low levels of impurities: sulphur and nitrogen compounds. Moreover, methane has the highest ratio of hydrogen to carbon compared to other hydrocarbons.

Another main application of complete combustion of methane is the abatement of its emission from natural gas or methane combustion devices. As methane is a potent greenhouse gas, 23 times more powerful at warming the atmosphere than carbon dioxide, it is important to reduce its amounts emitted into the atmosphere to mitigate in the short term the global warming.

Palladium based catalyst has shown a very high activity for the catalytic combustion of methane [1]. The aim of this work is to the study the promotion of complete oxidation of methane over palladium catalyst by using the phenomenon of Electrochemical Promotion, also called NEMCA effect (Non-Faraday Electrochemical Modification of Catalytic Activity). This concept was introduced and developed by the group of professor Vayenas more than 25 years ago [2,3]. This phenomenon allows improving the catalytic performance of a metal catalyst in a very pronounced and controlled way by application of low current or potentials through the catalyst–electrolyte interface. Thus, the work function is changed due to electrochemical pumping of ions from a solid electrolyte [4,5].

In this work, an oxygen ion conducting solid electrolyte (yttria-stabilized zirconia, YSZ) as the active catalyst support was studied in order to increase by electrochemical promotion the Pd activity for the catalytic combustion of methane. For the first time, the Pd catalyst film was prepared by direct impregnation onto the solid electrolyte, following a similar procedure reported elsewhere for Pt catalysts [6].

On the other hand, the modification of the YSZ support with ceria (CeO_2) was also studied. Ceria has been extensively employed as a textural and structural promoter for supported noble metal catalysts because of its unique redox properties and high oxygen storage capacity [7]. However, pure ceria shows a poor thermal stability. Thus, the combination of ZrO_2 and CeO_2 could lead to the improvement of not only its oxygen storage capacity, redox properties and catalytic activity but also the resistance to high temperatures [8]. The modification of Pd catalyst with ceria has been widely studied for conventional catalysts. But so far, NEMCA effect through ceria supports has been only explored in a work by the group of professor Vayenas [9].

2. Experimental

Pd/YSZ and Pd/CeO_2/YSZ were considered in this study as electrochemical catalysts. They consisted of a porous Pd film, with a geometric surface area of 2.01 cm^2, deposited on a side of a dense solid electrolyte disk of 8 mol% Y_2O_3-stabilized ZrO_2 (YSZ), 19 mm in diameter and 1 mm thick (Henson Ceramics Limited). Inert gold counter and reference electrodes were deposited onto the other side of the solid electrolyte by application of thin coatings of gold paste (Gwent Electronic Materials C1991025D2) followed by calcination at 800 °C for 1 h. Palladium films were prepared by

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successive steps of deposition and thermal decomposition of a palladium precursor solution as follows: 10 μl of the precursor, an aqueous solution of $[Pd(NH_3)_4](NO_3)_2$ with a concentration of 10 wt.% (Sigma–Aldrich), was applied onto the solid electrolyte using a plastic circle mask which defined the geometrical surface area of the catalyst-working electrode. Then, the solvent was evaporated at 100 °C for 10 min. After removing the mask, the sample was gradually heated at 450 °C for 1 h. This procedure of successive depositions, drying and heating was repeated to get the desired metal loading (1.1 mg Pd/cm^2). To prepare the Pd/CeO_2/YSZ catalyst, ceria was first impregnated on the YSZ support using a solution of $(NH_4)_2Ce(NO_3)_6$. Then, it was calcined at 600 °C for 1 h to get an oxide loading of 0.7 mg ceria/cm^2. After that, Pd was deposited on the same side following the procedure described above.

The dispersion of the catalyst–electrode film (fraction of active sites) was determined by the electrochemical technique developed by Ladas et al. [10]. The measured Pd surface was found to be 1.1 μmol for Pd/YSZ and 2.2 μmol for Pd/CeO_2/YSZ, leading to a metal dispersion of 6% and 11%, respectively. In addition, the electric resistance of the Pd catalyst-working electrode film was also checked with a digital multimeter UNI-T.

The catalytic experiments were carried out within a specific tubular quartz reactor (single chamber), as described in a previous work [11]. The electrochemical cell was placed on a fritted quartz with 20 mm of diameter, with the counter and reference electrode facing the fritted quartz. An inner quartz tube was pressed onto the Pd working electrode to insure electrical contact. The temperature of the catalyst was measured with a K-type thermocouple (Thermocoax) placed inside the inner quartz tube. The entire reactor was placed in a furnace (JH HEE.CC4) equipped with a heat control system (Conatec 4801). Constant potentials or currents across the cell were measured and imposed using a potentiostat–galvanostat Voltalab PGZ 301 (Radiometer Analytical). The reaction gases were Praxair certified standards of 4% CH_4/He, O_2, (99.99% purity), and He (99.999% purity), which was used as the carrier gas. The gas flow was controlled by a set of calibrated mass flowmeters (Brooks 5850 E and 5850 S). The feed composition was as follows: 4000 ppm CH_4, 10,000 ppm O_2, He balance, and the overall flow rate was 9 L h^{-1}. Reactants and products gases were analyzed with a CO_2/CO infrared gas analyzer (Fuji Electric Systems ZKJ-3) and a micro gas-chromatograph (Varian CP-4900). Prior to the catalytic activity measurements, the palladium film was stabilized with a thermal treatment under reactive mixture during 3 h at 700 °C. The contributions of homogeneous reaction, as well as the catalytic rate of methane combustion on both the pure solid electrolyte and gold electrodes were found to be negligible under operating conditions. Thus, all the potential-induced changes in the catalytic activity should be exclusively attributed to palladium. Carbon dioxide was the only C-containing product since CO and C_2-compounds were never detected.

Under closed circuit, measurements were performed under the potentiostatic mode. The rate enhancement ratio (ρ) of CO_2 was defined as

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

where r_0 is the catalytic reaction rate under open circuit conditions and r is the reaction rate under polarization.

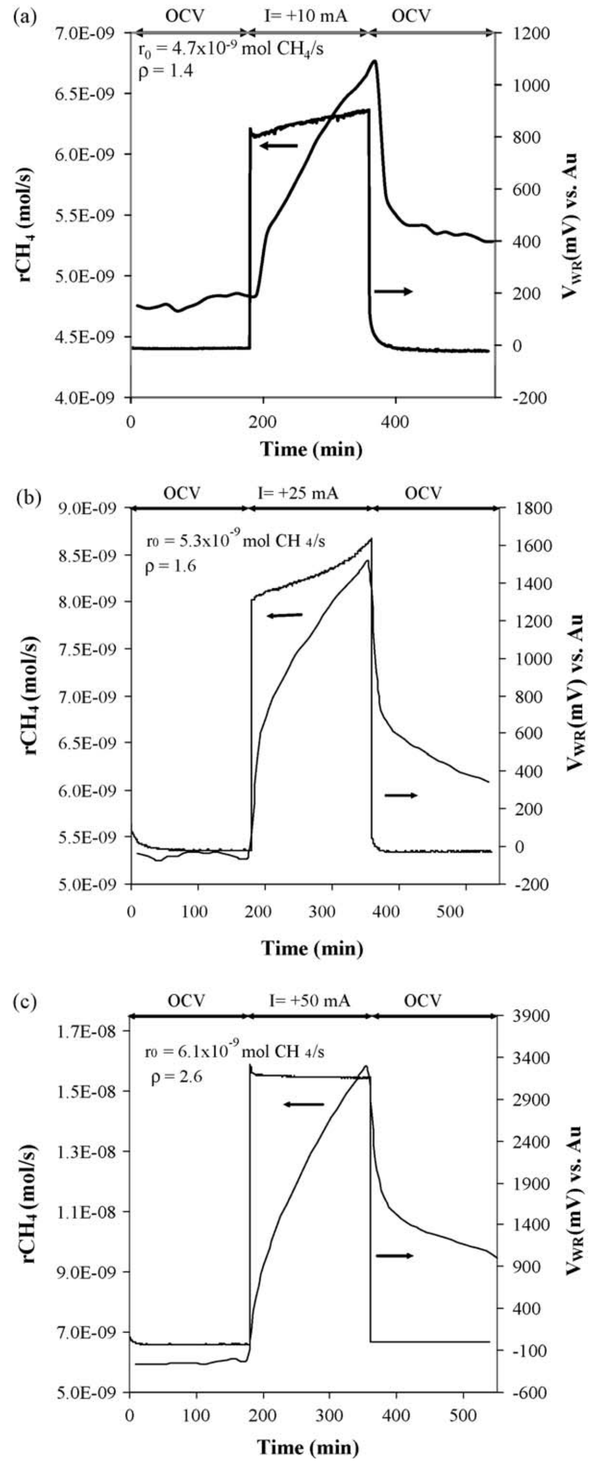

Fig. 1. Reaction rate r and catalyst potential response to a step change in applied current over Pd/YSZ, (a) I = 10 mA, (b) I = 25 mA. (c) I = 50 mA. Reaction conditions: T = 600 °C, CH_4 = 4000 ppm, O_2 = 10000 ppm, He balance, total flow rate = 9 L h^{-1}.

3. Results and discussion

3.1. Catalytic activity measurements over Pd/YSZ

For Pd/YSZ catalyst, the catalytic activity was investigated under atmospheric pressure and at 600 °C by galvanostatic transitions. Fig. 1 shows the response of the catalyst potential and CH_4 oxidation reaction rate upon imposition of a constant positive current between the palladium film and the counter electrode. For the first 3 h, the catalyst was under open circuit in order to stabilize it. Then, a constant current I was applied via the galvanostat so that O^{2-} ions were transferred from the solid electrolyte to the catalyst at a rate given by Fadaray's law, I/2F. Under open circuit conditions (OCV), the catalytic rate r_0 was found to be 4.7 × 10^{-9} mol CH_4/s (see Fig. 1a), while the catalyst potential was −12 mV. After current application (I = +10 mA), oxygen ions were transferred (at a rate $I/2\mathrm{F} = 5.2 \times 10^{-8}$ mol O/s), and a catalytic rate increase was observed (ρ = 1.4). The corresponding steady state potential value was about 850 mV. For the other applied currents, a similar behaviour was found, but the electrochemical parameter ρ increased with the current: ρ = 1.6 for I = +25 mA (Fig. 1b); and ρ = 2.6 for I = +50 mA (Fig. 1c) corresponding to a reaction rate enhancement of 60% and 160%, respectively. This behaviour implies that under anodic polarization an increase in the oxygen coverage surrounding the catalyst film involved a reaction rate increase. Therefore, the backspillover of electron acceptor species, i.e. oxygen ions, led to an increase in the catalyst work function and, hence, to an enhancement of the chemisorptive bond of electron donor adsorbates, i.e. methane [3]. Consequently, the catalytic reaction rate is increased by anodic polarization, exhibiting electrophobic behaviour. This is in good agreement with the results reported in previous works related to the electrochemical promotion of methane combustion [12–16].

On the other hand, it can be seen that for all the currents the catalytic reaction rate under open circuit after the anodic polarization was higher than that observed before. Therefore, a permanent promotional effect is observed. In order to check this behaviour, the catalytic activity was studied by a galvanostatic transient where the current (I = +30 mA) was applied for 6 h and the open circuit potential after the anodic polarization was measured for 10 h (Fig. 2). An electrochemical parameter ρ of 2.4 was obtained, higher than that observed in Fig. 1b for a similar current. In this case, a clear permanent effect was observed. That it could be attributed to the electrochemical metal oxidation. The supply of oxygen ions to the catalyst film could produce the oxidation of palladium; thus a higher amount of PdO species would be obtained. PdO has been shown to be the active phase for the Q1 reaction of methane oxidation [1,17]. Therefore, the permanent promotional effect observed would be due to extra formation of PdO after polarization.

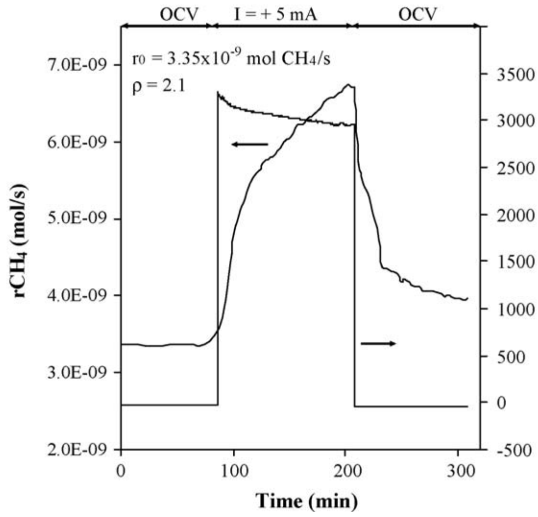

Fig. 3. Reaction rate r and catalyst potential response to a step change in applied positive current of I = 5 mA over Pd/CeO$_2$/YSZ. Reaction conditions: T = 470 °C, CH$_4$ = 4000 ppm, O$_2$ = 10000 ppm, He balance, total flow rate = 9 L h^{-1}.

3.2. Catalytic activity measurements over Pd/CeO$_2$/YSZ

The catalytic activity for the Pd/CeO$_2$/YSZ catalyst was investigated under atmospheric pressure at 470 °C by galvanostatic transitions. Fig. 3 shows the response of the reaction rate and potential when a current of 5 mA is applied. For this system, lower temperature and applied current were needed since it showed a catalytic activity higher than that of Pd/YSZ. The catalytic reaction rate under anodic polarization, where oxygen ions were transferred to the catalyst at a rate of $I/2\mathrm{F} = 2.6 \times 10^{-8}$ mol O/s, was found to be twice higher than that under open circuit potential (ρ = 2.1). The higher catalytic activity could be explained by the presence of ceria that would facilitate the strong improvement of the oxygen storage capacity due to a partial transformation of metallic palladium into PdO.

To confirm this point, both catalytic activity and electrochemical promotion effect over Pd/CeO$_2$/YSZ were analyzed by galvanostatic transitions carried out at the same conditions as shown in Fig. 1a; i.e. 600 °C and I = +10 mA. As seen in Fig. 4, the catalytic activity of palladium supported over CeO$_2$/YSZ under open circuit conditions ($r_0 = 6.59 \times 10^{-8}$ mol CH$_4$/s) was 14 times higher than that of Pd/YSZ. Consequently, Pd should be mainly found as PdO due to the high storage oxygen capacity of ceria.

It is also interesting to note that for this catalyst it was necessary to impose a potential of about 2700 mV to get a constant current of 10 mA, which is much higher than that used for Pd/YSZ. It means that the electric resistance shown by Pd/CeO$_2$/YSZ was higher due to presence of the ceria film and the lower conductivity of the PdO particles. Additionally, Pd/CeO$_2$/YSZ can still be promoted; a similar rate enhancement ratio (ρ = 1.6) as that for Pd/YSZ was obtained.

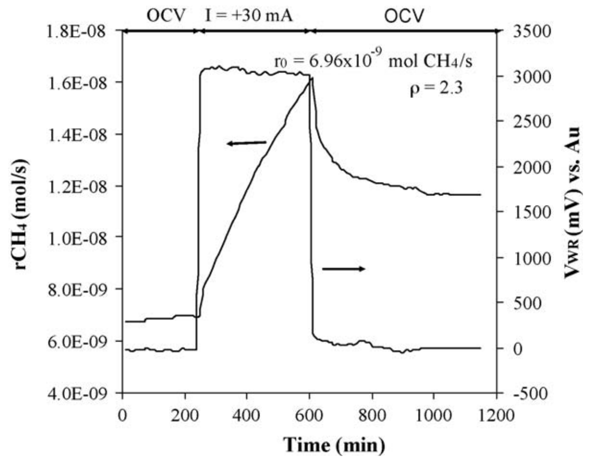

Fig. 2. Methane combustion reaction rate after an anodic polarization of I = 30 mA for 6 h. Reaction conditions: T = 600 °C, CH$_4$ = 4000 ppm, O$_2$ = 10000 ppm, He balance, total flow rate = 9 L h^{-1}.

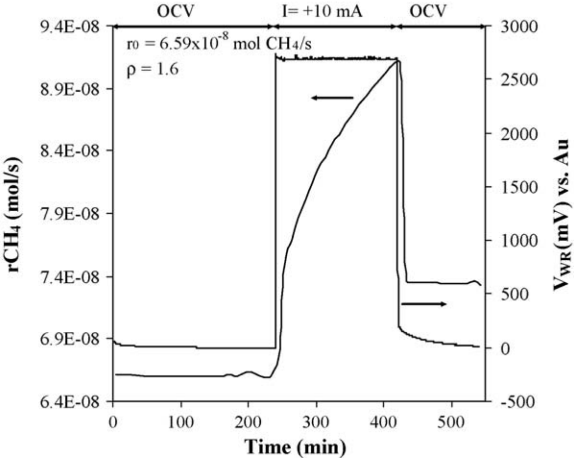

Fig. 4. Reaction rate r and catalyst potential response to a step change in applied positive current of I = 10 mA over Pd/CeO$_2$/YSZ. Reaction conditions: T = 600 °C, CH$_4$ = 4000 ppm, O$_2$ = 10000 ppm, He balance, total flow rate = 9 L h^{-1}.

Table 1
Influence of the reaction temperature on both the catalytic behaviour and the promotional parameters when Pd/CeO_2/YSZ was used as electrochemical catalyst under open circuit potential and promoted conditions (V_{WR} = +2 V and V_{WR} = +1 V). Reaction conditions: [CH_4] = 4000 ppm, [O_2] = 1%, He balance, total flow rate 9 L h^{-1}.

Temperature (°C)	r_0[a] ($\times 10^8$ mol CH_4/s)	V_{WR} = −1 V		V_{WR} = +1 V		V_{WR} = +2 V	
		r[b] ($\times 10^8$ mol CH_4/s)	ρ	r[b] ($\times 10^8$ mol CH_4/s)	ρ	r[b] ($\times 10^8$ mol CH_4/s)	ρ
470	0.33	0.27	0.82	0.40	1.33	0.42	1.30
600	8.13	7.85	0.97	8.55	1.05	8.75	1.08

[a] Reaction rate under open circuit conditions.
[b] Reaction rate under polarization conditions.

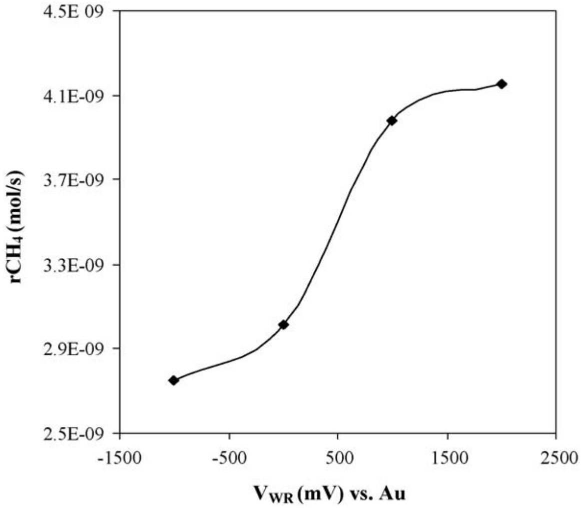

Fig. 5. Steady state effect of the applied catalyst potential (V_{WR}) on methane combustion reaction rate r over Pd/CeO_2/YSZ. Reaction conditions: T = 470 °C, CH_4 = 4000 ppm, O_2 = 10000 ppm, He balance, total flow rate = 9 L h^{-1}.

Table 1 compares the influence of the temperature on the methane combustion rate. It can be observed that the system presented the same behaviour under polarization as Pd/YSZ, i.e. electrophobic at high temperature. On the other hand, Fig. 5 shows the steady state effect of the applied potential on methane combustion rate. In this experiment, the potentiostat was set to impose a potential difference between the working and reference electrodes. The trend of the plot confirmed the electrophobic behaviour of the system. Thus, the catalytic reaction rate increased with positive polarizations while negative polarizations produced a decrease in the reaction rate.

Therefore, the promotional effect can be explained on the basis of two simultaneous phenomena: the proportion of PdO particles and the different coverage of the reactant species at varying catalyst potentials. Under negative polarization, the Pd═O bond is strengthened; thus the active sites are mainly covered by oxygen to the expense of methane. Under positive polarizations, there is a weakening of the Pd═O bond and, at the same time, methane adsorption is enhanced increasing the reaction rate.

4. Conclusion

The catalytic activity of palladium for the complete oxidation of methane can be increased via transference of oxygen ions from a solid electrolyte to the catalyst film. It can be explained by the different coverage of the reactant species under polarization, and by the transformation of metallic palladium into palladium oxide, thus increasing the number of active sites. The formation of additional PdO particles after polarization would be the reason of the permanent promotional effect observed for these catalysts.

Pd/CeO_2/YSZ catalyst showed a catalytic activity 14 times higher than that of Pd/YSZ, due to the well-known oxygen storage capacity of ceria and subsequent PdO formation. Anyway, it can still be electrochemically promoted, showing activity at one of the lowest reaction temperature reported for the electrochemical promotion of methane combustion.

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