In situ controlled electrochemical promotion of catalyst surfaces: Pd-catalysed ethylene oxidation

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Abstract

The catalytic activity of polycrystalline Pd films deposited on 8 mol % Y_2O_3-stabilized–ZrO_2 (YSZ), an O^{2-}-conductor, can be altered reversibly by varying the potential of the Pd catalyst film via the effect of nonfaradaic electrochemical modification of catalytic activity (NEMCA) or electrochemical promotion. The complete oxidation of ethylene was investigated as a model reaction in the temperature range 290–360 °C and atmospheric total pressure. The rate of C_2H_4 oxidation can be reversibly enhanced by up to 45% by supplying O^{2-} to the catalyst via positive current application. The steady-state rate change is typically 10^3–10^4 times larger than the steady-state rate $I/2F$ of electrochemical supply or removal of promoting oxide ions. The observed behaviour is discussed on the basis of previous NEMCA studies and the mechanism of the reaction.

1. Introduction

The rate and selectivity of catalytic reactions occurring on metal and metal-oxide porous catalyst films interfaced with solid electrolytes can be reversibly modified by electrochemical pumping of charged promoting species from the solid electrolyte to the catalyst surface where they alter the electronic properties (work function) and, concomitantly, the chemisorptive and catalytic properties of the latter. This effect of nonfaradaic electrochemical modification of catalytic activity (NEMCA) [1, 2] or electrochemical promotion [3] allows for *in situ* tuning of catalyst performance and has been reported for over fifty catalytic reactions on Pt, Rh, Pd, Ag, Fe, Ni, IrO_2 and RuO_2 surfaces on a variety of solid electrolytes including oxygen, sodium, fluorine and hydrogen ion conductors.

The first report of a nonfaradaic electrochemical effect on catalytic activity appeared in 1981 for the case of ethylene epoxidation on Ag [4], but it was only in 1988 when it was realized by Vayenas and coworkers [2] that electrochemical promotion is a general phenomenon. In addition to the latter group, several other research groups have made important contributions in this field [5–9]. Work in this area has been extensively reviewed [10, 11]. Electrochemically promoted catalytic rates up to 100 times higher than open-circuit (unpromoted) rates have been observed [10–12], which correspond to steady-state changes in catalytic rate exceeding the rate of electrochemical ion-transport by several orders of magnitude [10, 11, 13], typically by 10 to 10^5 times, thus exemplifying the non-faradaic nature of electrochemical promotion.

The results presented in this work concern the electrochemical promotion of Pd catalysts for the reaction of ethylene oxidation using 8 mol % Y_2O_3-stabilized–ZrO_2 (YSZ), an O^{2-}-conductor, as active catalyst support. Palladium is an important constituent of state-of-the-art three-way automotive exhaust catalysts where, along with Pt, is mainly used to control hydrocarbon and CO emissions [14]. Because of the high cost and limited availability, the optimization of the catalyst design and the reduction in the amount of palladium active phase, via appropriate promotion of its catalytic properties, is of significant importance. The choice of YSZ as the solid electrolyte support was dictated by the fact that this material is already used in car exhaust systems as the major component of the oxygen sensor and its long-term stability under operation conditions is known. The oxidation of C_2H_4 was chosen as a model hydrocarbon oxidation reaction, as the latter is known to exhibit a pronounced electrochemical promotion effect on other platinum group metals, such as Rh [12] and Pt [13]. To our knowledge, only a few studies pertaining to C_2H_4 oxidation on polycrystalline [15, 16] and single crystal [17, 18] Pd surfaces exist in literature, thus the open-circuit kinetics of the reaction were also studied. The investigation of the present system revealed similar electrochemical promotion behaviour to the one in the case of other platinum group metals, with catalytic rate changes exceeding the corresponding rate of ion transfer through the solid electrolyte (electrocatalytic rate) by a factor on the order of 10^3–10^4, although the attained catalytic activity change was much lower and did not exceed 70%.

2. Experimental details

The apparatus utilizing online gas chromatography and IR spectroscopy for continuous analysis of reactants and products has been described previously [13, 19]. The only products detected was CO_2 and H_2O. The reactor was a 'single-pellet' type [11] continuous flow atmospheric pressure reactor of volume 40 cm^3, exhibiting CSTR behaviour. The reactor was operated as a differential one, as the conversion of ethylene was kept below 10% both under open-circuit and closed-circuit conditions, and under conditions of absence of internal and external mass transfer limitations.

In this reactor an YSZ disc (3/4″ (19 mm) diameter, 2 mm thickness, Didier Werke AG), on which were deposited the Pd catalyst-electrode and two auxiliary Au electrodes, was suspended in the interior of a quartz tube via three gold wires that were used as electron collectors or suppliers and with the three electrodes all exposed to the reactive gas mixture. The porous Pd catalyst film (working electrode, W), with a superficial surface area of 0.4 cm^2, was deposited on one face of an YSZ disc using a thin coating of A1122 Engelhard Pd paste followed by calcination in air first at 400 °C for 2 h then at 900 °C for 10 h. The Au counter (C) and reference (R) electrodes, with superficial areas 1.0 cm^2 and 0.3 cm^2, respectively, were deposited on the other face of the solid electrolyte disc (the counter electrode opposite to the working electrode) using thin coatings of Demetron M8032 Au paste, followed by calcination in air first at 400 °C for 2 h then at 850 °C for 10 min. All electrodes were porous with thickness on the order of a few μm, as shown using scanning electron microscopy. Blank experiments showed that the catalytic rate of ethylene oxidation on the solid electrolyte and on the Au auxiliary electrodes was negligible.

The surface mol Pd of the catalyst films used in the present study (1.0×10^{-7} to 1.9×10^{-7} mol Pd) are presented in Table 1. They were measured via hydrogen chemisorption at 60 °C in the hydrogen pressure range 2–8 torr, after previous evacuation at 200 °C for 1 h and reduction at 300 °C for 2 h [20]. The amount of adsorbed hydrogen corresponding to monolayer coverage was determined by extrapolation to zero pressure [20] and an 1:1 hydrogen to palladium adsorption stoichiometry was assumed [20, 21]. The true surface areas of the Pd catalyst films (39 to 75 cm^2, Table 1) were estimated using as density of surface Pd atoms the one corresponding to Pd(1 1 1) face, that is, 1.53×10^{15} cm^{-2}. Small differences in the true surface

Table 1. Surface mol Pd (N) and true surface areas (A) of the catalyst films

Catalyst film	$10^7 N$ /mol Pd	A /cm^2
R1	1.0	39
R2	1.6	63
R3	1.9	75

areas of the Pd catalyst films (Table 1) are due to the different amount of deposited Pd catalyst in each case. Once the true surface area of a Pd catalyst film has been estimated, the surface areas of the other catalyst films were determined by comparing their steady-state catalytic activity with that of the original film at a set of standard conditions ($T = 340$ °C, $P_{O_2} = 10$ kPa, $P_{C_2H_4} = 2.5$ kPa). The measured surface mol Pd of the reduced catalysts were used to calculate turnover frequencies (TOF), that is, atoms of oxygen reacting per surface palladium atom per sec. However, it has to be noted that these surface mol Pd may not be exactly relevant to the measured catalytic activity, as under the reaction conditions of the present study the palladium catalyst can exist in oxidized form.

Constant currents, I, between the catalyst and the counter electrode (galvanostatic operation) or constant potentials, V'_{WR}, between the catalyst and reference electrode (potentiostatic operation) were applied via a galvanostat–potentiostat, as described elsewhere [13]. In order to determine the ohmic drop-free catalyst potential, V_{WR}, the parasitic ohmic component was determined using the current interruption technique [11, 13] and was subtracted from the corresponding V'_{WR} value.

3. Results

Figure 1 shows a typical NEMCA galvanostatic transient, that is, it depicts the response of the catalyst potential V'_{WR} and of rate r and turnover frequency (TOF) of C_2H_4 oxidation on Pd upon imposition of a constant positive current between the Pd catalyst and the counter electrode. At the beginning of the experiment ($t < 0$) no current is applied ($I = 0$) and the open-circuit catalytic rate is $r_o = 1.93 \times 10^{-7}$ mol O s^{-1} while the catalyst potential is equal to −100 mV. Then at $t = 0$ a constant current $I = 11$ μA is applied via the galvanostat and O^{2-} are transferred to the catalyst at a rate $I/2F = 5.70 \times 10^{-11}$ mol O s^{-1}. This causes a 44% increase in catalytic rate which stabilizes to a new value $r = 2.78 \times 10^{-7}$ mol O s^{-1} ($r/r_o = 1.44$). The corresponding steady-state value of catalyst potential V'_{WR} becomes 2030 mV. The rate increase $\Delta r = 0.85 \times 10^{-7}$ mol O s^{-1} is 1500 times larger than the rate of O^{2-} supply $I/2F$, that is, each O^{2-} supplied to the catalyst causes, on the average, 1500 additional chemisorbed oxygen atoms to react. Thus the system exhibits NEMCA behavior with corresponding enhancement factor or faradaic efficiency Λ equal to 1500, where Λ is defined from [1, 10, 11, 13]:

$$\Lambda = \Delta r \left(\frac{2F}{I} \right) \qquad (1)$$

The observed changes in catalytic rate and catalyst potential are quite reversible. Upon current interruption the catalytic rate and catalyst potential tend to relax to their open-circuit values. The potential transient is much
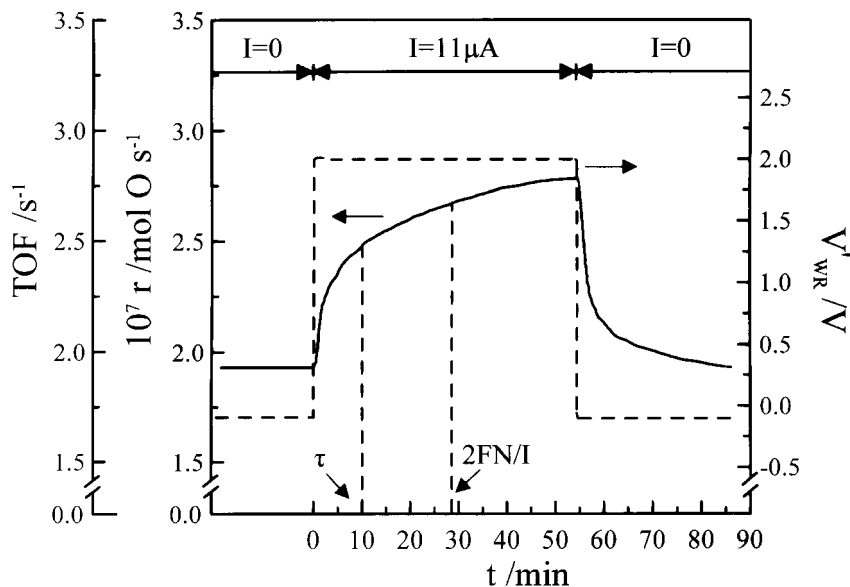
Fig. 1. Rate *r*, turnover frequency TOF and catalyst potential V'_{WR} response to a step change in applied positive current. Conditions: $T = 340$ °C, $P_{C_2H_4} = 2.5$ kPa, $P_{O_2} = 10$ kPa; catalyst R1 (see text for discussion).

faster than the rate transient for this system as also observed in earlier work where Pt catalyst was used [13]. The origin of this type of behaviour has been discussed previously [10].

The NEMCA time constant τ defined [10, 11, 13] as the time required for the rate change to reach 63% of its steady-state value during a galvanostatic transient is found to be in the present case equal to 10 min, in good qualitative agreement with the parameter $2FN/I = 29$ min, where $N = 1.0 \times 10^{-7}$ mol Pd is the surface mol Pd of the catalyst (corresponding to the true surface area of the catalyst film). This qualitative agreement is typical of electrochemical promotion studies utilizing YSZ and corroborates the theoretically [1, 10, 11, 13] and experimentally [22] well-established proposition that electrochemical promotion in this case is due to the electrochemically induced and controlled backspillover of $O^{\delta-}$ onto the catalyst surface and that these backspillover oxide ions act as promoters for the catalytic reaction. Similar transient behavior was observed in the case of negative current application, that is, a gradual decrease of the catalytic rate from its open-circuit value to a lower steady-state value corresponding to a nonfaradaic catalytic rate change.

Figure 2 shows the steady-state effect of applied current on the change in the rate of ethylene oxidation, expressed in mol O s^{-1}. Dashed lines are constant enhancement factor, Λ, lines. Enhancement factor or faradaic efficiency, Λ, values up to 16 000 (catalyst R2) were measured, that is, each O^{2-} supplied to the catalyst can cause on the average up to 16 000 chemisorbed oxygen atoms to react with ethylene. In agreement with all previous electrochemical promotion studies [10, 11] the order of magnitude of the measured Λ values is in good qualitative agreement with the parameter $2Fr_o/I_0$, where r_o is the open-circuit (unpromoted) catalytic rate
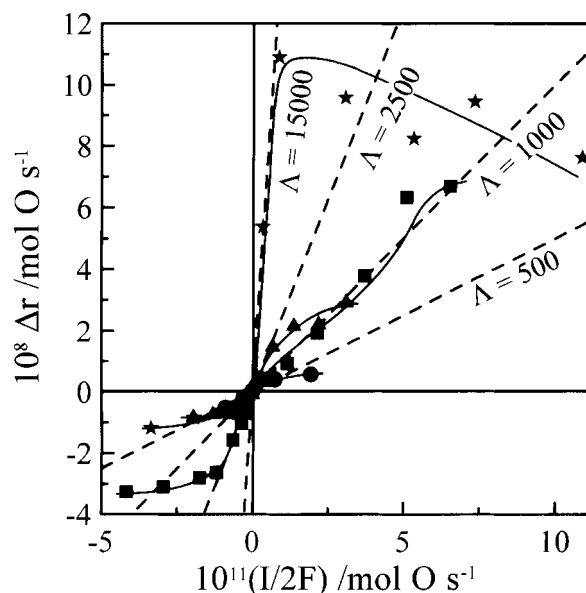

Fig. 2. Effect of applied current, *I*, on the induced change in the rate of C_2H_4 oxidation, Δr. Dashed lines are constant enhancement factor Λ lines. Conditions: $P_{O_2} = 10$ kPa, $P_{C_2H_4} = 2.5$ kPa; Catalyst R1. Key for *T*: (■) 340 °C, (▲) 320 °C, (●) 300 °C. Catalyst R2 (★) 340 °C. Open-circuit rates as in Table 2.

and I_0 is the exchange current [10, 11] of the catalyst–solid electrolyte interface. This is shown in Table 2, where are also presented the corresponding values of the open-circuit catalytic rate, r_o, and of the exchange current, I_0, extracted from current–overpotential plots [10, 11, 13]. The apparent activation energy of I_0 was found equal to 1.08 eV, in very good agreement with literature [23]. As shown in Figure 2, ethylene oxidation on Pd is an electrophobic reaction, that is, the catalytic rate decreases with negative current application and increases with positive current application (O^{2-} supply to the catalyst).

Table 2. Predicted ($2Fr_o/I_0$) and maximum measured (Λ_{max}) enhancement factor values (P_{O_2} = 10 kPa, $P_{C_2H_4}$ = 2.5 kPa)

Catalyst film	T/°C	$10^8\ r_o$/mol O s^{-1}	I_0/μA	$2Fr_o/I_0$	Λ_{max}
R1	300	6.84	0.6	22000	720
R1	320	8.61	1.0	16600	4700
R1	340	16.2	2.5	12500	2800
R2	340	26.5	3.6	14200	15700

Figure 3 shows the effect of varying ohmic-drop free catalyst potential, V_{WR}, and corresponding [1, 10, 11, 24] catalyst work function, $e\Phi$, on the catalytic rate enhancement ratio $\rho = r/r_o$ [10, 11, 13] at $P_{O_2} = 10$ kPa and $P_{C_2H_4} = 2.5$ kPa. The top axis in Figure 3 is based on the equality:

$$\Delta(e\Phi) = e\Delta V_{WR} \qquad (2)$$

established both theoretically [1, 10, 11, 13] and experimentally [1, 24] via *in situ* Kelvin probe measurements. As shown in Figure 3, by varying ohmic-drop free catalyst potential, V_{WR}, the rate enhancement ratio, $\rho(=r/r_o)$, varies approximately between 0.82 and 1.4. Equivalently, the catalytic rate increases by up to a factor of 1.7 ($=1.4/0.82$), as the work function, $e\Phi$, is increased by a few eV (e.g., 2 eV for catalyst R1 at $T = 340$ °C).

Figures 4 and 5 show the dependence of the steady-state rate and TOF on the partial pressures of ethylene $P_{C_2H_4}$ (0.3 to 6 kPa) (Figures 4(a) and 5(a)) and oxygen P_{O_2} (0.1 to 12.5 kPa) (Figures 4(b) and 5(b)) at different temperatures (290 to 360 °C) and under open-circuit
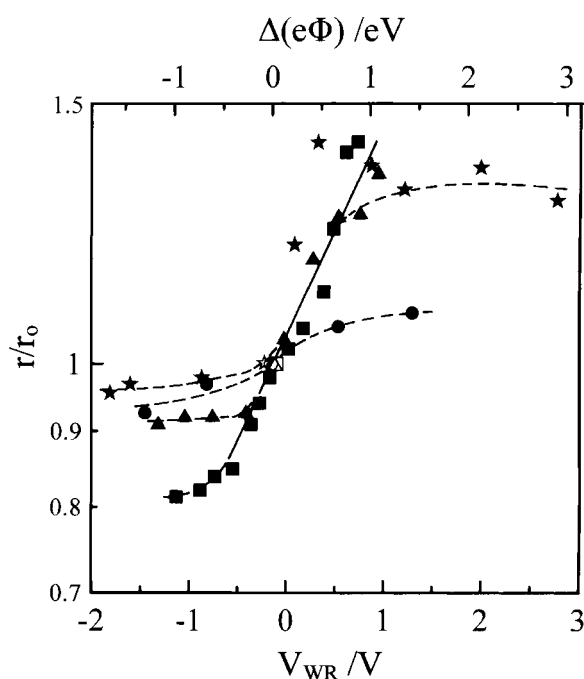

Fig. 4. Dependence of the open-circuit rate of C_2H_4 oxidation (expressed as O consumption rate) and turnover frequency, TOF: (a) on $P_{C_2H_4}$ at constant P_{O_2} (10 kPa), and (b) on P_{O_2} at constant $P_{C_2H_4}$ (2.5 kPa). Catalyst R3. Key for T: (■) 360, (◪) 340, (●) 320 and (△) 290 °C.

Fig. 3. Effect of applied ohmic-drop free catalyst potential V_{WR} and corresponding work function change $\Delta(e\Phi)$ (as calculated from Equation (2)) on the rate enhancement ratio $\rho = r/r_o$; Conditions as in Figure 2. Open symbols correspond to open-circuit conditions.
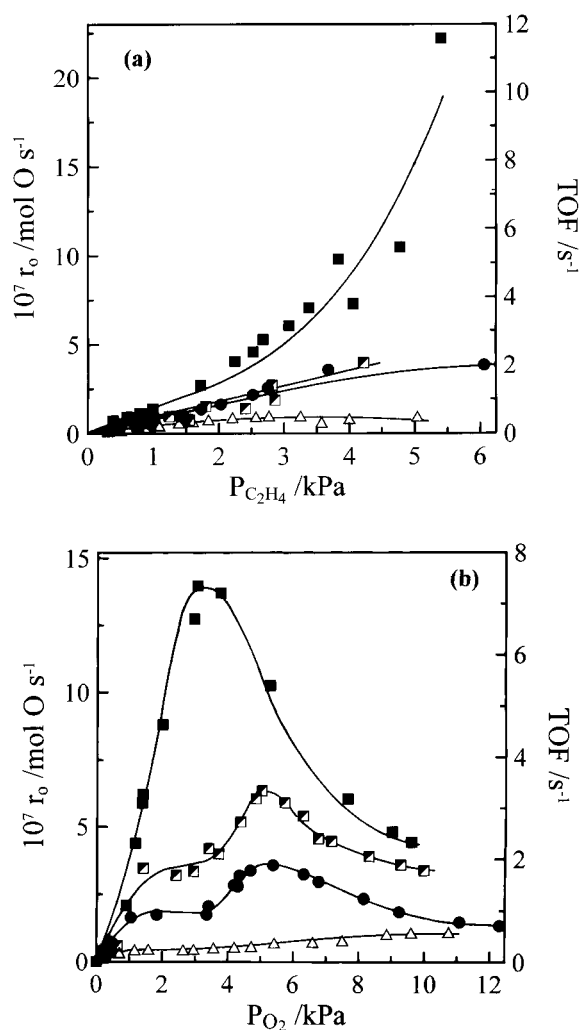
conditions (Figure 4) or when the catalyst potential V'_{WR} is maintained at -2 V or 1.5 V (Figure 5). As shown in Figure 4(a), for catalyst film R3, under open-circuit conditions and constant $P_{O_2} = 10$ kPa the rate is practically first order in ethylene at low $P_{C_2H_4}$ (less than 2 kPa), while at high $P_{C_2H_4}$ the apparent reaction order tends to increase from zero order at lower temperatures to higher than first order at 360 °C. On the other hand the dependence of catalytic rate on P_{O_2} under open-circuit conditions and constant $P_{C_2H_4} = 2.5$ kPa (Figure 4(b)) shows a Langmuir–Hinshelwood type kinetic behaviour, more clearly at higher temperatures, indicating competitive adsorption of C_2H_4 and O_2 on the catalyst surface, in agreement with previous studies [16]. The oxygen partial pressure $P_{O_2,max}$ at which the rate maximum is observed shifts gradually to lower values with increasing temperature. This shift indicates a higher heat of adsorption for oxygen than for ethylene, in agreement with literature [25, 26]. Interestingly, at 320 and 340 °C the rate maximum is preceded by a region of
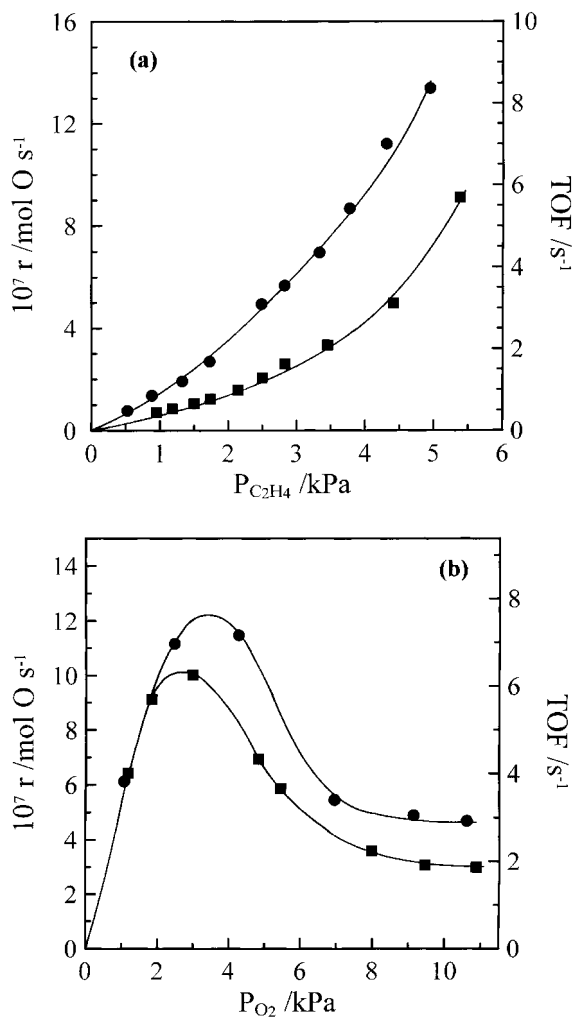
Fig. 5. Dependence of the rate of C_2H_4 oxidation (expressed as O consumption rate) and turnover frequency, TOF: (a) on $P_{C_2H_4}$ at constant P_{O_2} (11 kPa) and (b) on P_{O_2} at constant $P_{C_2H_4}$ (2.6 kPa) when the catalyst potential V'_{WR} is maintained at $+1.5$ V (●) and at -2 V (■). $T = 360$ °C; catalyst R2.

acceptor adsorbates, such as dissociatively chemisorbed oxygen [10, 11, 13, 27].

4. Discussion

The results reported in the present work establish that the catalytic activity of Pd for ethylene oxidation can be markedly affected via the NEMCA effect by using YSZ as an active catalyst support, meaning that the solid electrolyte can be used as promoter donor under conditions of polarization of the catalyst/solid electrolyte interface. Similarly to the cases of other platinum group metals, such as Rh [12] and Pt [13], interfaced with YSZ the effect can be attributed to the promoting action of oxide ions $O^{\delta-}$ which under conditions of positive polarization are forced to migrate (backspillover) onto the catalyst surface from the YSZ solid electrolyte [11, 22], thus altering the average work function $e\Phi$ of the catalyst surface (Equation 2) and affecting the binding strength of chemisorbed species [10, 11, 27–29] such as normally chemisorbed oxygen and ethylene. The existence of these charged backspillover species has been manifest on Pt catalyst-electrodes interfaced with YSZ using X-ray photoelectron spectroscopy (XPS) [22] and temperature-programmed desorption (TPD) [29], as well as on Pd catalyst-electrodes interfaced to YSZ using a.c. impedance spectroscopy [30]. This electrochemically-controlled migration (backspillover) is accompanied by nonfaradaic enhancement in the catalytic rate of ethylene oxidation, which demonstrates the promoting action of these backspillover species. As analysed elsewhere [12] and as shown by XPS [22] the backspillover oxide ions, the coverage of which can be as high as that of normally chemisorbed oxygen for high (>1V) applied potentials [22], can act as promoters because they are Λ ($\sim10^3$–10^4) times less reactive with C_2H_4 than normally chemisorbed oxygen. In the case of negative polarization, as there can be no backspillover oxide ions migration to the catalyst surface but only chemisorbed oxygen removal, the induced work function changes should be accommodated by changes in the coverages and/or the dipole moments of adsorbed species according to the Helmholtz equation [11]. Changes in the dipole moments of adsorbates can result from changes in their binding strength due to negative polarization and are accompanied by a concomitant readjustment in the surface coverages of oxygen and ethylene so that Equation 2 is satisfied.

Under the conditions of the electrochemical promotion experiments in the present study $P_{O_2} = 10$ kPa, $P_{C_2H_4} = 2.5$ kPa the rate is nearly first order in C_2H_4 and nearly zero order in oxygen (Figures 4 and 5), while the apparent activation energy, E_a, is under open-circuit equal to 0.65 eV, in excellent agreement with literature [15]. The observed reaction order implies that the Pd surface is here predominantly covered with oxygen and with very little adsorbed ethylene. The co-adsorption of oxygen and ethylene on metal surfaces favours the adsorption of ethylene in a π-bonded state [17, 18, 31],

constant rate, which becomes narrower with increasing temperature. This behaviour could be attributed to changes in the oxidative state of the catalyst surface in conjunction with different activities of palladium and palladium oxide for ethylene oxidation [15]. The observed behaviour is similar to the case of ethylene oxidation on Rh/YSZ [12], where abrupt rate variations were observed near the surface rhodium oxide stability limit. The absence of abrupt rate changes in the present case implies comparatively slower kinetics or different mode of palladium oxide formation/decomposition.

As shown on Figure 5(a) and (b), for catalyst film R2, the kinetic effect of the reactants remains qualitatively the same under closed-circuit (NEMCA) conditions, that is, the reaction mechanism does not change under conditions of electrochemical promotion. With increasing catalyst potential and work function the location of the rate maximum in Figure 5(b) seems to be shifted to higher P_{O_2} values, which indicates a weakening in the palladium–oxygen bond as expected for electron

which exhibits a pronounced electron donor character and a negligible backdonation of electron density from the metal surface [31]. Thus, under the conditions of the present study, chemisorbed ethylene is expected to exhibit electron donor behaviour. Increasing ohmic drop-free catalyst potential, V_{WR}, and work function, $e\Phi$, causes a weakening in the binding strength of electron acceptor adsorbates, such as dissociatively chemisorbed oxygen and a strengthening in the chemisorptive bond strength of electron donor adsorbates, such as chemisorbed ethylene [10–13, 27–29]. Both factors enhance the catalytic rate by decreasing the ratio of the surface coverages of oxygen to ethylene, $\theta_O/\theta_{C_2H_4}$, which tends to maximize the rate according to Langmuir–Hinshelwood kinetics. At the limit of very high V_{WR} this ratio approaches unity, as manifested both in Figure 2 and in Figure 3 where the rate approaches a plateau with increasing current and V_{WR}, respectively. The observed NEMCA behaviour could also be partly attributed to increase of the apparent kinetic constant with increasing catalyst potential, as the variation in the binding strength of chemisorbed reactive species is expected to affect both the apparent activation energy of the catalytic reaction, if the rds involves cleavage of chemisorptive bonds, and the apparent preexponential factor, which depends on the mobility of chemisorbed species and on the relative amounts of chemisorbed oxygen and ethylene.

Comparison of the results of electrochemical promotion of Pd for ethylene oxidation to the case of other platinum group metals can be made on the basis of the corresponding values of promoting index P_i of oxide ions, where P_i is defined from [11]:

$$P_i = \frac{\Delta r/r_o}{\Delta\theta_{O^{\delta-}}} \tag{3}$$

The coverage $\theta_{O^{\delta-}}$ of the oxide ions at steady-state can be estimated by analysis of the rate transient (Figure 1) upon current interruption [19] and was found here equal to 0.16. By using the values $\Delta\theta_{O^{\delta-}} = 0.16$ and $\Delta r/r_o = 0.44$ (Figure 1) a value equal to ∼3 can be calculated for the promotion index P_i of the oxide ions for C_2H_4 oxidation on Pd. This value is close to the P_i values obtained in the case of ethylene oxidation on Rh/YSZ [12] provided that the comparison is confined to the conditions of the present study, that is, temperatures below 350 °C and oxidative gaseous composition, which assure that the catalyst surface is and remains oxidized both under open- and closed-circuit conditions. The high P_i values (up to 90) observed with positive current application in the case of C_2H_4 oxidation on Rh/YSZ [12] under oxidative gaseous composition and temperatures higher than 350 °C have been attributed to reduction of the surface Rh oxide and to the concomitant pronounced rate enhancement.

In the case of C_2H_4 oxidation on Pt/YSZ [13] P_i values up to 60 have been observed under conditions similar to the ones of the present study. This difference could be attributed to variations in the way and strength of oxygen chemisorption on these two metals. It is well established that oxygen is strongly bonded onto the Pd surface forming a stable surface or subsurface (incorporated) metal oxide layer [15, 25, 32, 33], the presence of which has been recently invoked to explain the polarization behavior of the O_2–Pd–YSZ interface [23]. Thus the relative effect of altering catalyst potential and work function on the strength of the metal–oxygen bond is here not so pronounced as in the case of Pt [13], where loosening of the metal-oxygen bond with increasing catalyst potential increases the catalytic rate by decreasing significantly the activation energy of the rate determining step of the reaction of C_2H_4 with chemisorbed oxygen [13]. The previous argument is also corroborated by the results of a recent study of C_2H_4 oxidation on Pd/β''–Al_2O_3 [34], where were also observed relatively low catalytic activity changes (up to 120%) and electrophobic behaviour by changing catalyst potential and, thus, by altering the surface coverage of electrochemically migrating promoting sodium species.

5. Conclusions

This study demonstrates that, similar to other platinum group metals, the catalytic activity of Pd for the complete oxidation of ethylene can be reversibly affected via the effect of nonfaradaic electrochemical modification of catalytic activity (NEMCA) or electrochemical promotion by interfacing polycrystalline Pd films with 8 mol % Y_2O_3-stabilized–ZrO_2 (YSZ), an O^{2-}-conductor, and varying the potential of the Pd catalyst film. In the temperature range 290 to 360 °C the reaction exhibits electrophobic NEMCA behaviour over the entire potential range, that is, the rate of CO_2 formation increases (by up to 70%) with increasing catalyst potential or work function, while the steady-state rate change is typically 10^3–10^4 times larger than the steady-state rate $I/2F$ of electrochemical supply or removal of O^{2-} to or from the catalyst. Although the induced rate changes are not spectacular, the present results allow for useful comparisons to other platinum group metals and could be useful in the design of more effective automotive catalytic converters.

Acknowledgements

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