JOURNAL OF APPLIED ELECTROCHEMISTRY **25** (1995) 978–981

Electrochemical promotion of IrO_2 catalyst for the gas phase combustion of ethylene

E. VARKARAKI, J. NICOLE, E. PLATTNER, CH. COMNINELLIS*

Institute of Chemical Engineering, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland

C. G. VAYENAS

Department of Chemical Engineering, University of Patras, Patras GR 26500 Greece

Received 15 January 1995; revised 13 March 1995

The catalytic activity of IrO_2 catalyst films for the gas phase combustion of ethylene can be increased by up to a factor of 10 via anodic polarization of the IrO_2 catalyst relative to a Au electrode both deposited on Y_2O_3-stabilized ZrO_2 solid electrolyte. The steady-state increase in the catalytic reaction rate is typically 200 higher than the expected rate increase of ethylene combustion calculated from Faraday's law. This is the first demonstration of the effect of non-faradaic electrochemical modification of catalytic activity (NEMCA) using a metal oxide catalyst.

1. Introduction

Regulatory pressure is increasing to reduce emissions of volatile organic compounds (VOC) to the atmosphere. Two main techniques are commonly used for the treatment of VOC; incineration and biological treatment [1]. The use of biological treatment is limited to readily biodegradable compounds in contrast to incineration which can be used for the treatment of a variety of VOC [2]. Commercial incineration systems fall, basically, into two types, straight thermal incineration at about 900 °C or catalytic incineration at about 500 °C.

In this paper the complete oxidation of ethylene as a model VOC pollutant to CO_2 has been studied on an IrO_2 film deposited on a ceramic solid electrolyte [Y_2O_3-stabilized ZrO_2 (YSZ)]. Recently Vayenas and coworkers [3–8] have shown that the catalytic activity and selectivity of metal catalysts deposited on solid electrolytes can be altered in a dramatic manner by applying potential or current to the metal catalyst using a counter and a reference electrode.

2. Experimental details

In all experiments a three-electrode cell was used (Fig. 1). The electrolyte was a thin rectangular plate (26 mm × 13 mm and 1 mm thick) of 6 mol % Y_2O_3-stabilized ZrO_2 (YSZ). Gold paste counter (50 mm^2) and reference (10 mm^2) electrodes were deposited on one side of the plate.

The IrO_2 working electrode was deposited on the other side of the plate using the thermal decomposition technique [9]. In this technique 3 μl of the solution containing the precursor (0.093 M H_2IrCl_6 in isopropanol) was applied on the YSZ followed by drying (80 °C) and calcinating in air for 1 h at 550 °C. The mass of the IrO_2 electrode was 63 μg and its superficial surface area was 0.5 cm^2. The Au counter and reference electrodes were also exposed to the reacting gas mixtures. Blank experiments showed that the catalytic rate on these electrodes is negligible. The experimental apparatus shown schematically in Fig. 2 utilizes online gas-chromatography (Shimadzu GC-8A) and i.r. spectroscopy (Siemens, Ultramat 5E-2R) for continuous analysis of the reactor feed and products. Oxygen and C_2H_4 were diluted in ultrapure He (99.999%). Their partial pressure in the reaction medium was $P_{O_2} = 18$ kPa and $P_{C_2H_4} = 0.12$ kPa, respectively.

A galvanostat-potentiostat (EG&G, Princeton Applied Research model 362) was used for galvanostatic transients and for cyclic voltammetric measurements.

3. Results and discussion

The temporal evolution of the rate of C_2H_4 combustion (expressed in g-atoms of oxygen per second) during a typical galvanostatic step (100 μA applied for 200 min) is shown in Fig. 3. In the same Figure the expected reaction rate (calculated from Faraday's law for the combustion of C_2H_4) is also given.

Initially ($I = 0$) the circuit is open and the rate of C_2H_4 combustion on the IrO_2 catalyst is very slow (Equation 1)

$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O \qquad (1)$$

After the application of a constant current ($I = 100\,\mu$A, rate $I/2F$ of O^{2-} supply to the catalyst equal to 1.04×10^{-9} g-atoms O s^{-1}), the rate of C_2H_4 combustion starts increasing and within 200 min gradually reaches a value which is five times larger than the initial rate. The catalytic rate increase

---

* To whom correspondence should be addressed.

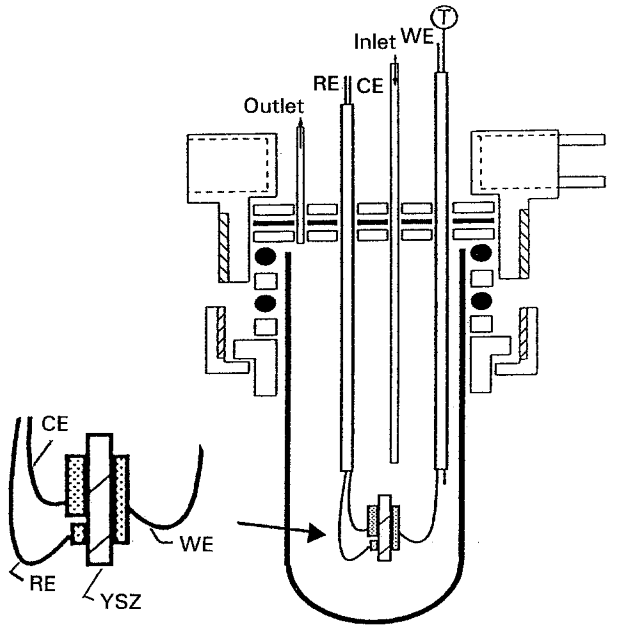

Fig. 1. Reactor configuration: (WE) working electrode (IrO_2), (CE) counter electrode (Au), (RE) reference electrode (Au), (YSZ) solid electrolyte (6 mol % Y_2O_3-stabilized ZrO_2) and (T) thermocouple.

is 200 times larger than the expected rate increase of C_2H_4 combustion calculated from Faraday's law (Fig. 3). This is why this effect, which was first discovered with metal catalysts [3–8], has been termed non-faradaic electrochemical modification of catalytic activity (NEMCA).

Figure 3 shows also that upon current interruption the rate of C_2H_4 combustion decreases slowly and finally returns to its initial value.

The variation of the IrO_2 catalyst potential (against the reference electrode in contact with the same reaction medium) during the galvanostatic step is also given in Fig. 3.

To study the influence of current on the rate of C_2H_4 combustion it is useful to define an enhancement factor Λ from

$$\Lambda = \frac{2F}{I}(r - r_0) = \frac{2F}{I}\Delta r \qquad (2)$$

where r_0 denotes the open-circuit catalytic rate, r the steady state catalytic rate after application of a constant current I and F is Faraday's constant.

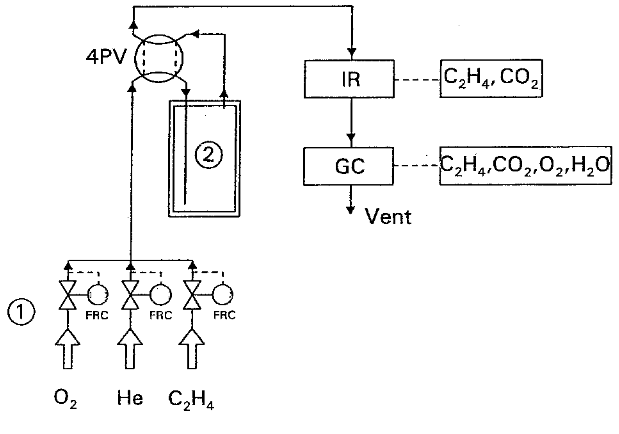

Fig. 2. Schematic diagram of the apparatus: (1) feed unit and (2) reactor (see Fig. 1).

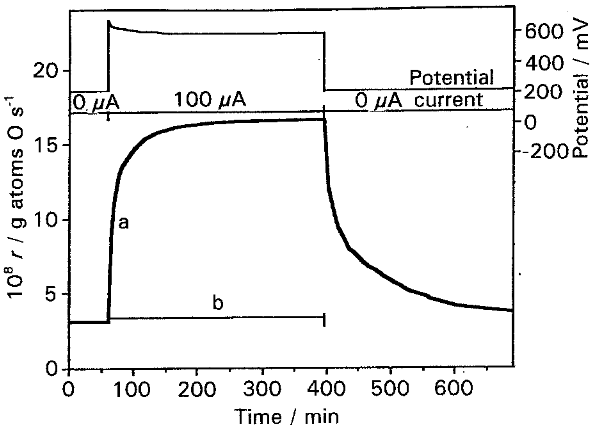

Fig. 3. Combustion of C_2H_4 at the IrO_2 catalyst. Rate and catalyst potential response to a typical galvanostatic step. $T = 380\,°C$, $P_{O_2} = 18\,kPa$, $P_{C_2H_4} = 0.12\,kPa$. Key: (a) Experimental rate and (b) theoretical rate calculated from Faraday's law.

The increase in the catalytic rate (Δr) was measured for different applied currents (I) and the enhancement factor Λ was calculated from Equation 2. Figure 4 compares the experimental increase in the catalytic rate (Δr) with those calculated from Faraday's law. The results shown in Fig. 4 were obtained with excess oxygen. Under these conditions and for low applied current ($I/2F < 8 \times 10^{-10}$ g-atoms O s^{-1}) oxygen adsorption on the surface of the IrO_2 catalyst is near equilibrium and the rate of the reaction is controlled by the surface reaction between chemisorbed oxygen and C_2H_4.

Under these conditions, the reaction is first order in C_2H_4 and zeroth order in oxygen:

$$r = kP_{C_2H_4} \qquad (3)$$

where k is a kinetic constant and $P_{C_2H_4}$ is the partial pressure of C_2H_4. By further increasing the current ($I/2F > 1 \times 10^{-9}$ g-atoms O s^{-1}), the rate of C_2H_4 combustion reaches a plateau. In this region it is likely that oxygen chemisorption [3, 6] or diffusion of C_2H_4 to the catalyst surface become rate limiting.

Figure 5 shows the same data presented in Fig. 4 but in terms of $\ln(r/r_0)$, (where r_0 is the open circuit

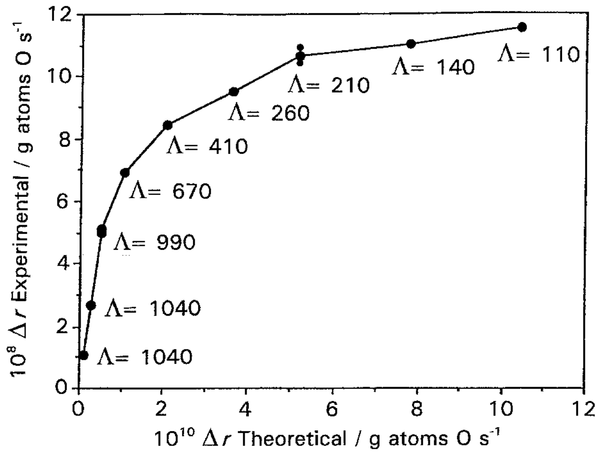

Fig. 4. Combustion of C_2H_4 at the IrO_2 catalyst. Comparison between the experimental increase in the catalytic rate (Δr) with the theoretical rate increase ($\Delta r = I/2F$) calculated from Faraday's law. Enhancement factor, Λ, was calculated from Equation 2. $T = 380\,°C$, $P_{O_2} = 18\,kPa$, $P_{C_2H_4} = 0.12\,kPa$.

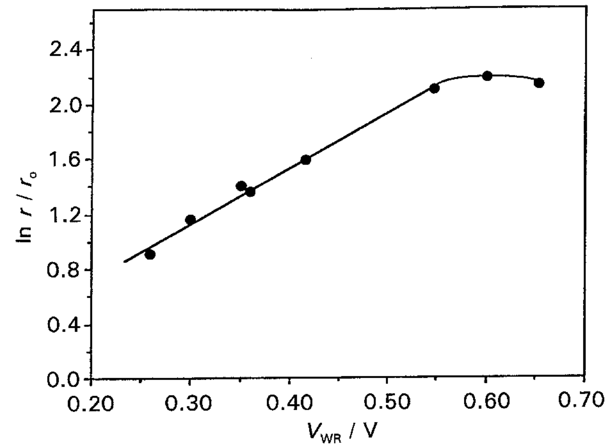

Fig. 5. Effect of catalyst potential (relative to the reference electrode) on the rate of C_2H_4 combustion. Conditions as in Fig. 4.

catalytic rate) against catalyst potential V_{WR} (relative to the reference electrode); r depends exponentially on the catalyst potential as in NEMCA studies on metal catalysts [3–8]:

$$\ln\left(\frac{r}{r_0}\right) = \frac{\alpha F \Delta V_{WR}}{RT} \qquad (4)$$

with $\alpha = 0.23$. For the present system, this exponential increase continues until the point where the rate reaches a plateau.

To investigate the origin of the NEMCA effect on the IrO_2 film, cyclic voltammetry was used in the potential region where the electrochemical reduction of gaseous oxygen (Equation 5) occurs to a negligible extent:

$$O_2(g) + 4e^- \Leftrightarrow 2O^{2-} \qquad (5)$$

Figure 6 shows a typical cyclic voltammogram obtained at $50\,mV\,s^{-1}$. The charges involved in the anodic and cathodic sweeps of the voltammogram are practically equal.

The anodic or cathodic voltammetric charge q^* obtained by integration of the cyclovoltammetric curve has been found to be 1.9×10^{-4} C for freshly prepared IrO_2 which corresponds to $680\,C\,mol^{-1}$ IrO_2 at $50\,mV\,s^{-1}$. Taking into account that the 'width' δI of the cyclic voltammogram under the present conditions is $2vC_d$ [10], where v is the scan rate and C_d is the capacitance of the electrode-electrolyte interface, $C_d = 300\,\mu F$ is obtained from Fig. 6. Taking into account that the superficial electrode–electrolyte surface area is $0.5\,cm^2$, this corresponds to a specific double-layer capacitance C'_d of $600\,\mu F\,cm^{-2}$. This value is a factor of 2 to 3 higher than those measured for the Pt–YSZ interface at temperatures 600 to 800 °C using the a.c. impedance method [11–13].

Regarding the origin of this voltammetric charge q^* it is evident that it involves interfacial (IrO_2 catalyst/YSZ solid electrolyte) reactions and surface diffusion processes on the IrO_2 film. It is presumed that the voltammetric charge q^* provides a measure of the amount of O^{2-} exchanged with the YSZ solid electrolyte according to the reaction:

$$IrO_2 + \delta O^{2-} \Leftrightarrow IrO_{2+\delta} + 2\delta e^- \qquad (6)$$

The excess oxygen (δ) in the oxide film is transported by surface diffusion on the gas exposed IrO_2 film. To correlate the voltammetric charge, q^*, with the rate of C_2H_4 oxidation (Equation 1) the following experiment was carried out: The IrO_2 catalyst was polarized anodically (relative to the gold counter electrode) by application of a constant current $100\,\mu A$ and the rate of C_2H_4 oxidation to CO_2 was monitored. After 200 min of anodic polarization, the current was interrupted and cyclic voltammograms were run at consecutive time intervals. At the same time the rate of CO_2 formation was measured. Figure 7 shows that there is a linear relation between the voltammetric charge q^* and the rate of C_2H_4 combustion. This result confirms that the origin of NEMCA is directly related to an additional storage of electrical charge in the catalyst film (at the catalyst–YSZ interface) which is compensated by the additional storage of an equal and opposite charge in the YSZ solid electrolyte. Since the fermi level (or electrochemical potential of electrons $\bar{\mu}$) in the metal catalyst is and remains spatially uniform in the catalyst film during NEMCA experiments [7, 8], the above observation is consistent with the observed work function increase on the gas-exposed catalyst-electrode surface under NEMCA conditions [7, 8]. This is because no net charge can be stored at the electrode gas interface [7], and thus the volta potential Ψ of the electrode surface remains zero. Since

$$e\Delta V_{WR} = -\Delta\bar{\mu} = \Delta(e\Phi) + \Delta(e\Psi) \qquad (7)$$

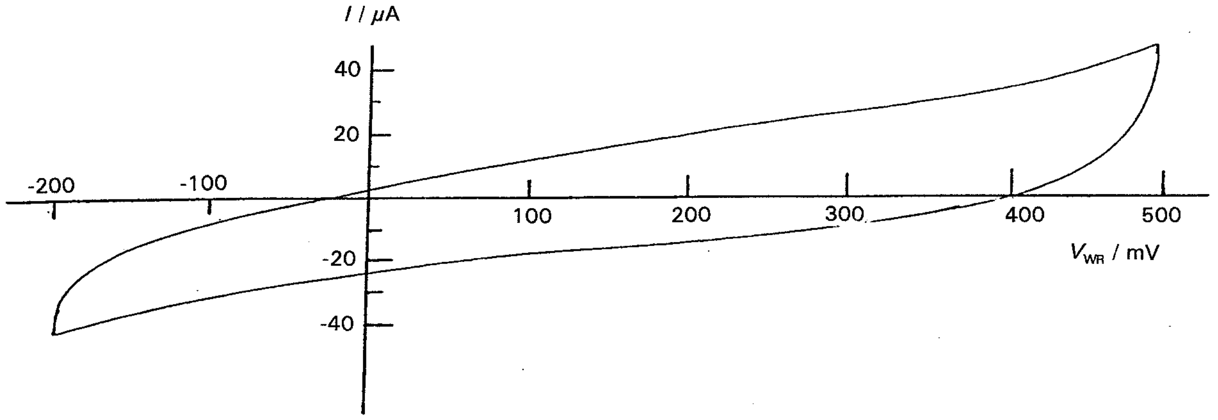

Fig. 6. Typical cyclic voltammogram of the IrO_2 catalyst. Scan rate: $50\,mV\,s^{-1}$. Conditions as in Fig. 4.

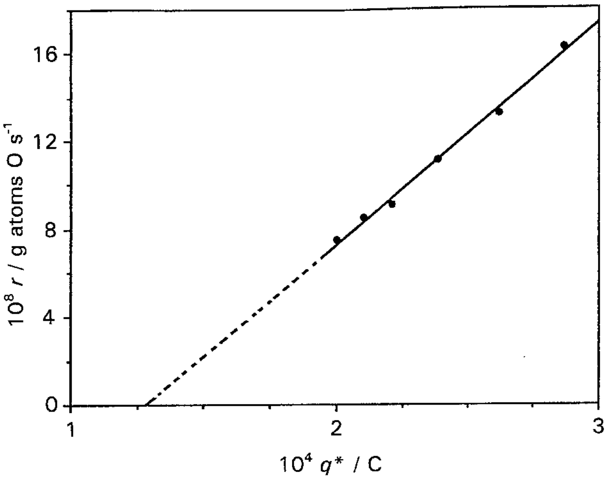

Fig. 7. Relation between voltammetric charge q^* and the rate of C_2H_4 combustion. Conditions as in Fig. 4.

it follows that the work function $e\Phi$ of the electrode surface must increase by $e\Delta V_{WR}$ [7]. Thus, the observed behaviour can be explained as follows.

When the IrO_2 catalyst (working electrode) is polarized anodically relative to the gold electrode (counter electrode), oxygen gas is reduced at the gold electrode near the YSZ–Au–gas phase three phase boundaries, producing oxygen anions (Equation 8):

$$\tfrac{1}{2}O_2(g) + 2e^- \longrightarrow O^{2-} \qquad (8)$$

Under the influence of the electric field in the YSZ, O^{2-} migrate towards the YSZ–IrO_2 interface and are oxidized forming $IrO_{2+\delta}$ [9], the so called higher oxide [14] (Equation 6).

This higher oxide [14] formed at the YSZ–catalyst interface is transported by surface diffusion onto the gas-exposed catalyst surface. The excess charge in the IrO_2 catalyst is compensated by an equal and opposite excess charge in the YSZ solid electrolyte. This extra charge, measured via cyclic voltammetry in the present investigation, is consistent with the observed work function increase, under positive polarization on the gas-exposed electrode surface under NEMCA conditions with metal electrodes [7, 8]. In this case the work function increase is due to the migration (backspillover) of oxide ions from the YSZ solid electrolyte on the gas-exposed catalyst surface [5]. In the present case the work function increase must be due to the formation of surface $IrO_{2+\delta}$ via surface migration of O^{2-}. The catalytic activity on $IrO_{2+\delta}$ is higher than on IrO_2 and this causes the observed pronounced and reversible catalytic rate enhancement.

Acknowledgement

We thank Drs I. V. Yentekakis and Y. Jiang for their assistance in the early experiments.

References

[1] M. Woodfield and W. Spring, *Env. Protect. Bull.* **10** (1991) 25.
[2] A. Thompson, *ibid.* **10** (1991) 17.
[3] C. G. Vayenas, S. Bebelis and S. Neophytides, *J. Phys. Chem.* **92** (1988) 5083.
[4] I. V. Yentekakis and C. G. Vayenas, *J. Catal.* **111** (1988) 170.
[5] S. Ladas, S. Kennon, S. Betelis and G. G. Vayenas, *J. Phys. Chem.* **97** (1993) 8845.
[6] S. Bebelis and C. G. Vayenas, *J. Catal.* **118** (1989) 125.
[7] C. G. Vayenas, S. Bebelis, I. V. Yentekakis and H.-G. Lintz, *Catalysis Today* **11** (1992) 303.
[8] C. G. Vayenas, S. Beblis and S. Ladas, *Nature* **343** (1990) 625.
[9] Ch. Comninellis and G. P. Vercesi, *J. Appl. Electrochem.* **21** (1991) 335.
[10] A. J. Bard and L. R. Faulkner, 'Electrochemical methods: fundamentals and applications', J. Wiley & Sons, New York (1980).
[11] D. Y. Wang and A. S. Nowick, *J. Electrochem. Soc.* **126** (1979) 1166.
[12] M. J. Verkerk and A. J. Burgraaf, *J. Electrochem. Soc.* **130** (1983) 76
[13] A. J. A. Winnubst, A. H. A. Scharenborg and A. J. Burgraaf, *Solid State Ionics* **14** (1984) 319.
[14] Ch. Comninellis, *Electrochim. Acta* **39** (1994) 1857.