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

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The catalytic activity for the gas phase combustion of ethylene of an IrO_2 film, used as electrode in a solid electrolyte cell, can be increased by polarizing the metal–solid electrolyte interface. The catalytic activity remains higher even after current interruption. To explain the increase in the open circuit rate after polarization we speculate that the IrO_2 catalyst is oxidized at the catalyst–solid electrolyte interface, forming $IrO_{2+\delta}$, which is transported by surface and/or bulk diffusion to the gas exposed catalyst, thus modifying its catalytic activity.

Keywords: *ethylene*, *IrO_2 catalyst*, *gas phase combustion*, *electrocatalysis*, *solid electrolyte*, *electrochemical activation*

1. Introduction

Reduction of emissions of volatile organic compounds (VOC) to the atmosphere is an important current problem, especially due to increased regulatory pressures. The two main techniques used for the treatment of VOC are incineration and biological treatment [1]. The use of biological treatment must be limited to readily biodegradable compounds while incineration can be used for the treatment of a variety of VOCs [2]. Industrial incineration systems may be split into two types: thermal oxidation at about 900 °C and catalytic oxidation at about 500 °C.

Recently, Vayenas and coworkers [3, 4] have shown that the catalytic activity of metal catalysts deposited on solid electrolytes can be altered in a dramatic manner by applying potential or current to the metal catalyst. Very recently, it has been shown [7] that the catalytic activity of iridium oxide 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 gold electrode both deposited on Y_2O_3-stabilized ZrO_2 solid electrolyte. The steady-state increase in the catalytic reaction rate is typically 200 times higher than the calculated rate increase in ethylene combustion from Faraday's law [7, 8].

In this paper the complete oxidation of ethylene as a model VOC pollutant to CO_2 has been further studied on an IrO_2 film deposited on a ceramic solid electrolyte (Y_2O_3-stabilized–ZrO_2 (YSZ)). The results show that the application of an anodic current for a given time to the oxide catalyst using a counter and a reference electrode, can increase the reaction rate even after interruption of the current. This activation by electrochemical pretreatment under given conditions can be two to three times higher than the initial activity of the catalyst.

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 [5]. 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 calcination 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 gold counter and reference electrodes were also exposed to the reacting gas mixture. Blank experiments showed that the catalytic rate of ethylene combustion on the gold counter electrodes is negligible.

The experimental apparatus, shown schematically in Fig. 2, utilizes online gas chromatography (Shimadzu GC-8A) and infrared spectroscopy (Siemens, Ultramat 5E-2R) for continuous analysis of the reactor feed and products. Oxygen and ethylene were diluted in ultrapure helium (99.999%). Their partial pressure in the reaction medium was $P_{O_2} = 17$ kPa and $P_{C_2H_4} = 0.14$ kPa, respectively. The reaction temperature was maintained at 380 °C.

A galvanostat/potentiostat (EG & G, PAR, model 362) was used for galvanostatic transients. Application of a galvanostatic step to the IrO_2 catalyst modifies its open circuit activity. In order to obtain reproducible results, before each galvanostatic step,

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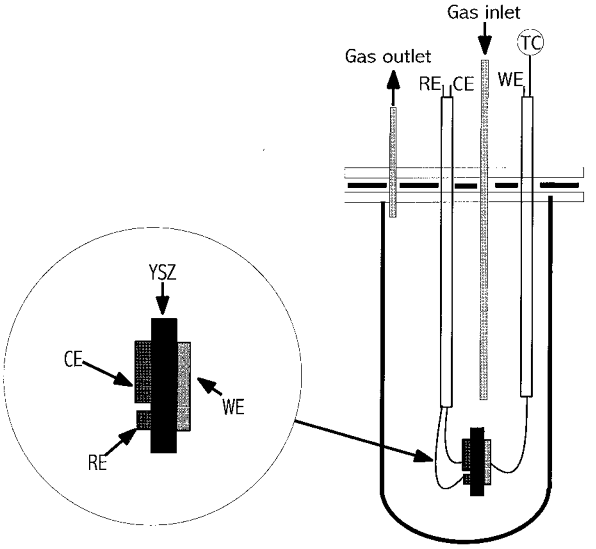

Fig. 1. Reactor configuration: (WE) working electrode (IrO_2); (CE) counter electrode (Au); (RE) reference electrode (Au); (YSZ) solid electrolyte (6 mol% Y_2O_3 stabilized ZrO_2); (TC) thermocouple.

ethylene diluted in helium ($P_{C_2H_4} = 1.00$ kPa) was fed to the reactor for 20 min at 380 °C. After this treatment the IrO_2 catalyst was restored to its initial open circuit activity.

3. Results

The time dependence of the rate of C_2H_4 combustion at 380 °C (expressed in mol of oxygen per second) during a typical galvanostatic step (300 μA applied for 120 min) and after current interruption is shown in Fig 3. In the same figure, the variation of the IrO_2 catalyst potential (vs the gold reference electrode in contact with the same reaction medium) during the galvanostatic step is given.

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

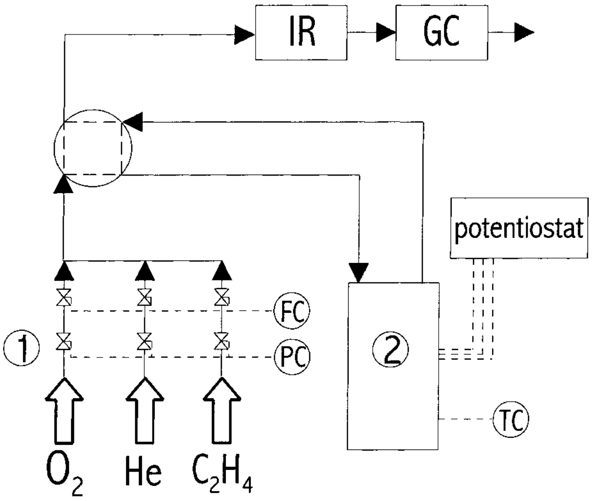

Fig. 2. Schematic diagram of the apparatus: (1) feed unit, (2) reactor (see Fig. 1). (IR) infrared analyser; (GC) gas chromatograph.

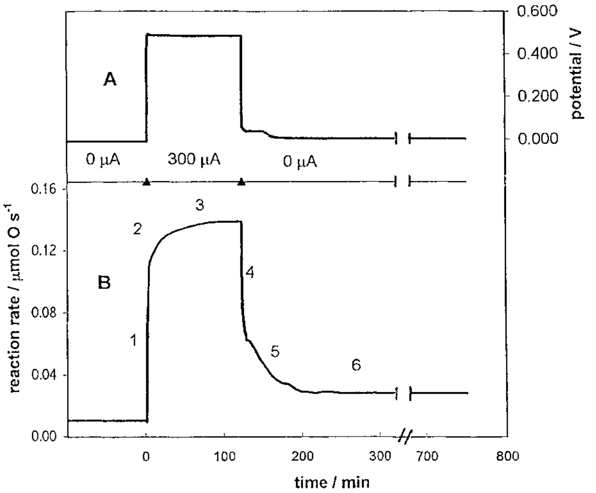

Fig. 3. Combustion of C_2H_4 at the IrO_2 catalyst. Catalyst potential (A) and rate (B) response to a typical galvanostatic step of 300 μA during ethylene oxidation on IrO_2. 1 to 6 show the six characteristic regions (see text). Conditions: $T = 380\,°C$, $P_{O_2} =$ 17 kPa, $P_{C_2H_4} = 0.14$ kPa.

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

After the application of a constant current ($I = 300\,\mu$A, rate $I/2$ F of O^{2-} supply to the catalyst is equal to 1.55×10^{-9} mol O s^{-1}), the rate of ethylene combustion increases and within 120 min gradually reaches a value 13 times larger than the initial rate. The catalytic rate increase is about two orders of magnitude higher than the expected increase in the ethylene combustion rate calculated from Faraday's law. Further examination of the response of IrO_2 catalyst to the galvanostatic step shows the presence of six regions (Fig. 3).

In region 1, the rate of ethylene combustion after current application increases rapidly and within less than 2 min reaches a value which is about eight times higher than the initial rate (this corresponds to 60% of the steady-state increase). After this rapid increase, the reaction rate increases slowly (region 2) reaching finally steady-state (region 3) after about 90 min. The rate of ethylene combustion after current interruption decreases rapidly (region 4) and within few minutes reaches a value which is about 40% of the steady state increase. Finally, the rate of ethylene combustion decreases slowly (region 5), reaching steady state (region 6).

Figure 3 also shows that the rate of ethylene combustion in region 6 is about three times higher that the initial rate for more than 10 h without any tendency to decrease. The similarity between regions 1 and 4 and regions 2 and 5 indicates that similar mechanisms are involved during current application and current interruption, but the fact that the steady-state rate of ethylene combustion after current interruption is higher than the initial rate indicates that the phenomena is not completely reversible. The increase in the catalytic activity of an IrO_2 catalyst after current interruption (region 6 in Fig. 3) is observed only if the catalyst is treated with ethylene before the

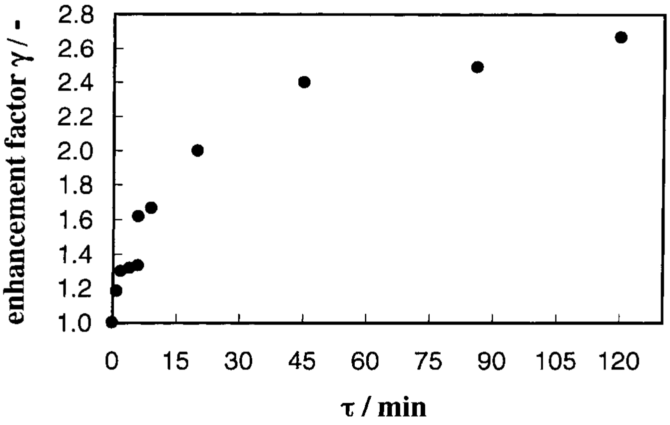

Fig. 4. Influence of the duration (τ) of the galvanostatic step on the enhancement factor γ (Equation 2). Conditions as in Fig. 3.

galvanostatic step (see experimental part). For better understanding the phenomena of the electrochemical activation of IrO_2 catalyst, the duration (τ) of the galvanostatic steps was varied and the open circuit rate of ethylene combustion in region 6 (Fig. 3) was measured.

Figure 4 shows the influence of τ on the rate enhancement γ defined by

$$\gamma = r/r_0 \tag{2}$$

where r_0 and r denote the steady-state open-circuit catalytic rate of ethylene combustion before and after a galvanostatic step, respectively. As shown in Fig 4, the enhancement ratio, γ, increases with the galvanostatic step duration, reaching a plateau for a polarization of about 90 min.

It is interesting to note here that the enhancement ratio γ, defined by Equation 2, is close to 1 ($\gamma \simeq 1$) if the duration of the galvanostatic step (τ) lies in the boundary of region 1 (Fig. 3). A typical example is given in Fig. 5.

These results show clearly that the electrochemical activation of IrO_2 catalyst is a two stage process: a rapid reversible stage (the IrO_2 catalyst restores its initial activity after the galvanostatic step, i.e., $\gamma = 1$), followed by a slow irreversible stage (the activity of the IrO_2 catalyst is increased after the galvanostatic step, i.e., $\gamma > 1$).

To confirm the presence of a first rapid reversible stage, successive galvanostatic steps were applied to IrO_2 catalyst and the rate of ethylene combustion was followed. A typical example is given in Fig. 6 in which five successive galvanostatic steps (300 μA during 1 min followed by 1 min open circuit) were applied to IrO_2 catalyst (A). In the same figure the rate of ethylene combustion after application of a galvanostatic step during 5 min (B) is also given. Comparison of curves A and B in Fig. 6 (in both cases the same amount of electricity was used) shows that in case A, where the galvanostatic step lies in region 1, the catalyst is restored to its initial activity after the galvanostatic step ($\gamma = 1$), contrasting with case B (the galvanostatic step reaches region 2) where the open-circuit activity of the IrO_2 catalyst is increased ($\gamma = 1.7$).

4. Discussion

The electrochemical activation of metal catalysts (Ag, Pt), used as electrodes in high temperature solid

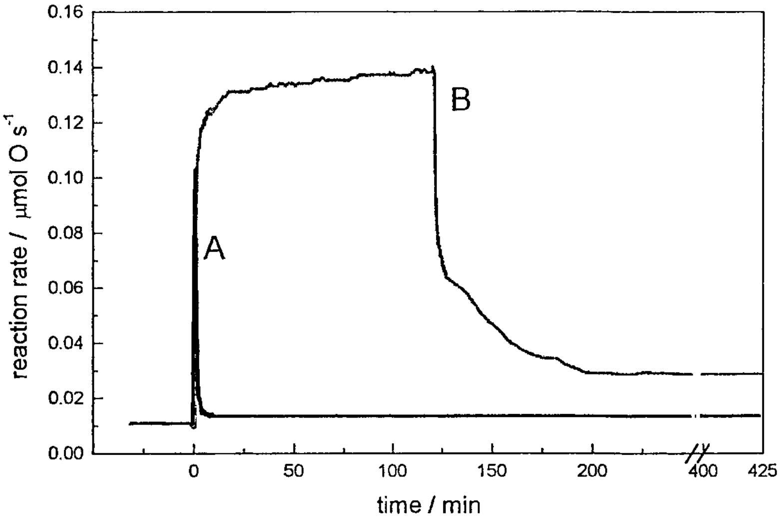

Fig. 5. Influence of the duration of the galvanostatic step on the rate of ethylene combustion. Duration of the galvanostatic step: (A) 1 min and (B) 120 min. Conditions as for Fig. 3.

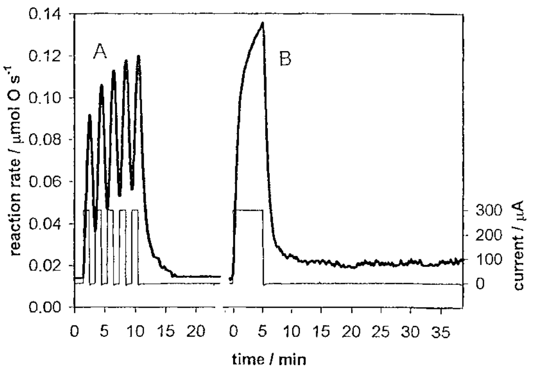

Fig. 6. Rate response of ethylene combustion (bold line) to galvanostatic pulses (normal line) (A) 5 steps of 300 μA during 1 min followed by 1 min open circuit, and to a galvanostatic step (B) 300 μA during 5 min. Conditions as in Fig. 3.

electrolyte, was discovered in 1988 by Vayenas and coworkers [3, 4]. In his pioneer work, Vayenas proposed a mechanism which is based on the spill-over of electrochemically formed active oxygen, from the solid electrolyte onto the metal catalyst. According to Vayenas, the effect is catalytic and takes place over the entire gas exposed catalyst surface [4]. The results presented in this paper using IrO_2 catalyst show that the activation of the IrO_2 catalyst after current application is a two-stage process: (a) a fast (few minutes) and reversible stage, and (b) a slow (few hours) and irreversible stage.

The following model is proposed to explain this two stage activation of IrO_2 catalyst. When the IrO_2 catalyst (working electrode) is polarized anodically relative to the gold electrode (counter electrode), an electric double layer is formed at the IrO_2/YSZ interface. This layer is composed of a positive charge on the IrO_2 catalyst and a negative charge in the YSZ electrolyte.

Under these conditions, O^{2-} ions are discharged at the YSZ–IrO_2 interface according to the reaction

$$O^{2-} \longrightarrow O^- + e^- \qquad (3)$$

This O^- ions produced at the YSZ–IrO_2 interface migrate toward the gas exposed catalyst surface. This causes an increase in the work function of the gas-exposed IrO_2 catalyst surface resulting in an increase in the activity of the catalyst. The rate of migration of O^- species is not limited by surface diffusion but rather by the rate of their creation. This explanation is the same as given by Vayenas using metal catalyst [4] and corresponds to the fast and reversible stage observed with IrO_2 catalyst in this work.

To explain the slow stage, we speculate that the O^- ions at the YSZ/IrO_2 interface interact with the IrO_2, forming a higher oxide $IrO_{2+\delta}$ at the catalyst/solid electrolyte interface:

$$IrO_2 + \delta O^- \longrightarrow (IrO_{2+\delta})_{IrO_2/YSZ} \qquad (4)$$

This higher oxide is transported by surface and/or bulk diffusion onto the gas exposed catalyst surface:

$$(IrO_{2+\delta})_{IrO_2/YSZ} \longrightarrow (IrO_{2+\delta})_{IrO_2/gas} \qquad (5)$$

The slow increase (region 2 in Fig. 3) in the rate of C_2H_4 combustion, observed after the initial fast increase can be explained by the slow modification of the gas-exposed catalyst due to surface diffusion of $IrO_{2+\delta}$ (Equation 5). The catalytic activity for ethylene combustion on $IrO_{2+\delta}$ is higher than on IrO_2 and this causes the observed catalytic rate enhancement.

After current interruption, the O^- ions present at the gas exposed catalyst surface react rapidly with ethylene resulting in an immediate decrease in the reaction rate of ethylene combustion (region 4 in Fig. 3), reaching a value which is about 40% of the steady-state value. The remaining high catalytic activity (region 5 in Fig. 3) is due to the presence of $IrO_{2+\delta}$ at the IrO_2/YSZ interface and on the gas-exposed catalyst. The fact that there is a linear relation between the voltammetric charge (which provides a measure of the amount of O^{2-} exchanged with the YSZ solid electrolyte forming $IrO_{2+\delta}$) and the rate of ethylene combustion [7] consolidates our model. The observed slow decrease in the rate of ethylene combustion is due to the consumption of $IrO_{2+\delta}$ for ethylene oxidation. When all the gas-exposed $IrO_{2+\delta}$ is consumed, the rate of ethylene combustion is constant (region 6 in Fig. 3) but remains higher than the initial rate. The fact that the IrO_2 catalyst can be restored to its initial activity, only after cathodic polarization or after treatment with excess ethylene in the absence of O_2, indicates that $IrO_{2+\delta}$, which is not easily accessible (present in the micropores of the catalyst or at IrO_2/YSZ interface), is responsible for observed remaining increase of catalytic activity relative to the initial value.

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