# In Situ Controlled Promotion of Catalyst Surfaces via Solid Electrolytes: Ethylene Oxidation on Rh and Propylene Oxidation on Pt

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Abstract. The kinetics of C_2H_4 oxidation on Rh and C_3H_6 oxidation on Pt were investigated on polycrystalline metal films interfaced with $ZrO_2(8mol\%Y_2O_3)$ solid electrolyte in galvanic cells of the type:

$$C_2H_4, O_2, Rh / YSZ / Pt, O_2 \text{ and}$$
$$C_3H_6, O_2, CO_2, Pt / YSZ / Au, C_3H_6, O_2, CO_2$$
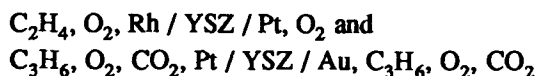
It was found that by applying positive potentials and thus, supplying O^{2-} to the catalyst surface, up to 100-fold increases in catalytic rate can be obtained (electrophobic NEMCA effect) for the case of C_2H_4 oxidation on Rh. For the case of C_3H_6 oxidation on Pt, up to 6-fold increases in catalytic rate were observed by negative potentials, i.e. removing of O^{2-} from the catalyst surface (electrophilic NEMCA effect).

The induced changes in catalytic rates for both reactions were found to be 10^3 to 5×10^4 higher than the rates of ion transfer to or from the catalyst-electrode surface.

For both reactions it was found that varying the catalyst potential, and thus work function, causes pronounced changes in activation energy and preexponential factor, leading to an interesting demonstration of the well-known "compensation" effect.

The results can be rationalized on the basis of the theoretical considerations invoked to explain previous NEMCA studies, i.e. the effect of changing work function on chemisorptive bond strengths of electron acceptor and electron donor adsorbates.

1. Introduction

During the last six years the effect of non-Faradaic electrochemical modification of catalytic activity (NEMCA) [1-18] or in situ controlled promotion of catalyst surfaces [19,20] has been described for over twenty-five catalytic reactions on Pt, Pd, Ag and Ni surfaces using O^{2-}-conducting solid electrolytes, such as yttria-stabilized-zirconia (YSZ) [1-9,14-18], Na^+-conducting solid electrolytes, such as $\beta"-Al_2O_3$ [10,20] and H^+-conducting solid electrolytes, such as $CsHSO_4$ [21] and F^--conducting solid electrolytes, such as CaF_2 [22] as the active catalyst support. Work prior to 1992 has been reviewed [2]. Very recently the effect has been demonstrated in aqueous electrochemistry [23].

When using YSZ as the solid electrolyte, NEMCA is due to the promoting action of spillover oxide ions $O^{\delta-}$ as originally proposed [2,5] and as recently confirmed by XPS [24]. For the latter it was found that the promoting oxide ion on Pt has an O1s binding energy of 528.8 eV vs 530.0 eV for normally chemisorbed oxygen which coexists on the surface [24].

The enhancement factor or Faradaic efficiency, Λ, is defined by:

$$\Lambda = \Delta r/(I/2F) \tag{1}$$

where Δr is the induced change in catalytic rate expressed in mol O, I is the applied current, and F is Faraday's constant. A reaction exhibits the NEMCA effect when $|\Lambda| > 1$. When $\Lambda > 1$ the reaction is termed electrophobic

(C_2H_4/O_2/Rh in this study), while when $\Lambda<-1$ the reaction is termed electrophilic (C_3H_6/O_2/Pt in this study).

The NEMCA effect can be explained by taking into account the effect of the potentiostatically or galvanostatically controlled back-spillover of promoting species from the solid electrolyte onto the gas-exposed catalyst surface and the effect of these species on the binding strength of chemisorbed reactants and intermediates [2].

Over wide ranges of catalyst work function $e\Phi$ (0.1-1.0 eV), which can be controlled easily by potenstiostatically controlling the coverage of the promoting species on the catalyst surface, catalytic rates, r, depend exponentially on $e\Phi$:

$$\ln(r/r_o) = \alpha \left(e\Phi - e\Phi^*\right)/k_bT \qquad (2)$$

where r_o is the open-circuit (unpromoted) catalytic rate and α, $e\Phi^*$ are reaction - and catalyst - specific constants. The parameter a usually takes values between -1 and 1 ($\alpha>0$ for electrophobic reactions and $\alpha<0$ for electrophilic ones)

In the present study we present results of the NEMCA behaviour of C_2H_4 oxidation on Rh and of C_3H_6 oxidation on Pt. Both reactions are found to exhibit a very pronounced NEMCA effect and also a NEMCA-induced compensation effect. In the case of C_2H_4 oxidation on Rh the measured $r(r/r_0)$ values are the highest observed so far in NEMCA studies.

2. Experimental

The NEMCA studies during C_3H_6 oxidation were carried out in a "single pellet" type reactor, i.e. a YSZ disc was suspended in a quartz well mixed reactor with the three electrodes, i.e., catalyst, counter and reference, all exposed to the reacting gas mixtures. A series of blank experiments was conducted without Pt catalyst and showed no influence to the catalytic rates due to the presence of Au under all operating conditions.

For the experiments of C_2H_4 oxidation the metal working catalyst electrode was deposited on the inner surface of a ceramic solid electrolyte tube (i.e. Y_2O_3-stabilized-ZrO_2 (YSZ), an O^{2-} conductor).

The catalyst electrode is exposed to the reactive gas mixture in a continuous-flow gradientless reactor.

For both cases under open-circuit conditions (I=0) the polycrystalline films act as regular catalysts.

The electrodes are connected with a galvanostat/ potentiostat which is used to apply constant currents

between the catalyst and the counter electrode or constant potentials between the catalyst and reference electrode. In this way O^{2-} ions are supplied from (or to) the solid electrolyte to (or from) the catalyst-electrode surface. The current is defined positive when anions are supplied to the catalyst electrode.

Experimental details for testing the catalysts under reaction conditions and details of catalyst, counter and reference electrode preparation and characterization have been reported extensively elsewhere [2,20].

3. Results and Discussion

3.1 NEMCA studies for the C_2H_4/O_2/Rh system.

The kinetics of C_2H_4 oxidation were investigated on polycrystalline Rh films interfaced with ZrO_2 (8 mol% Y_2O_3), or YSZ, solid electrolyte in a galvanic cell of the type: C_2H_4, O_2, Rh/YSZ/Pt, O_2. It was found that by applying external potentials and thus supplying O^{2-} to the catalyst surface, up to 100-fold increases in catalytic rate are obtained.

An example is presented in Fig. 1 which shows a typical galvanostatic transient, i.e., it depicts the transient effect of a constant applied current on the rate of C_2H_4 oxidation and on catalyst potential, V_{WR}. At the start of the experiment ($t\leq0$) the circuit is open (I=0) and the steady state catalytic rate value, r_0, is 1.8×10^{-8} mol O/s. At t=0 the galvanostat is used to apply a constant current (I=400 μA) between the catalyst and the counter electrode. According to Faraday's Law, oxygen anions are supplied to the catalyst at a rate $G_O=I/2F=2.05\times10^{-9}$ mol
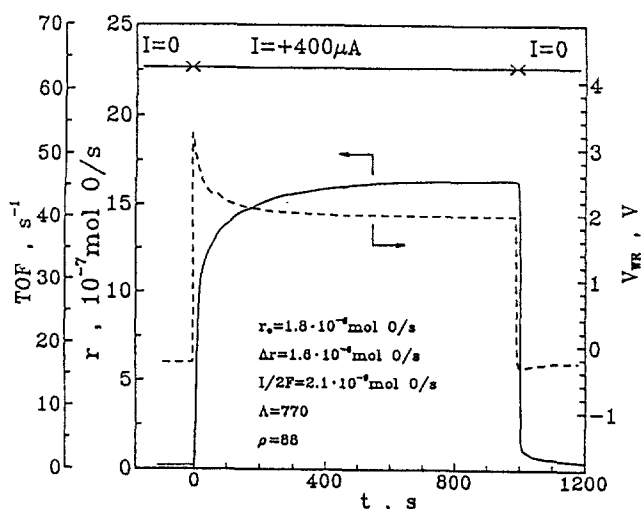

Fig.1. A galvanostatic transient during C_2H_4 oxidation on Rh. Conditions: $P_{O_2}^o$=2.6 kPa, $P_{C_2H_4}^o$=5.9 kPa, T=350°C.
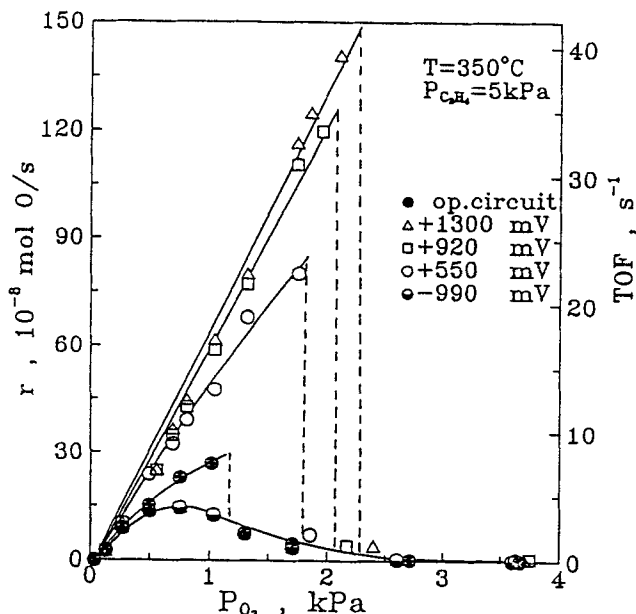
Fig. 2. Effect of P_{O_2} and catalyst potential on the rate of C_2H_4 oxidation on Rh.

O/s. This causes an 8800% increase in catalytic rate ($\Delta r = 1.6 \times 10^{-6}$ mol O/s). The rate increase Δr is 770 times larger than the rate of supply of oxygen anions G_O ($\Lambda = 770$). This means that each O^{2-} supplied to the catalyst causes, at steady state, 770 chemisorbed oxygen atoms to react and form CO_2. In the present work the maximum observed value of Faradaic efficiency Λ, was of the order of 5×10^4.

The kinetic behavior upon varying catalyst potential is shown in Figs. 2 and 3. The kinetics of the reaction seem to exhibit an abrupt discontinuity. This sharp
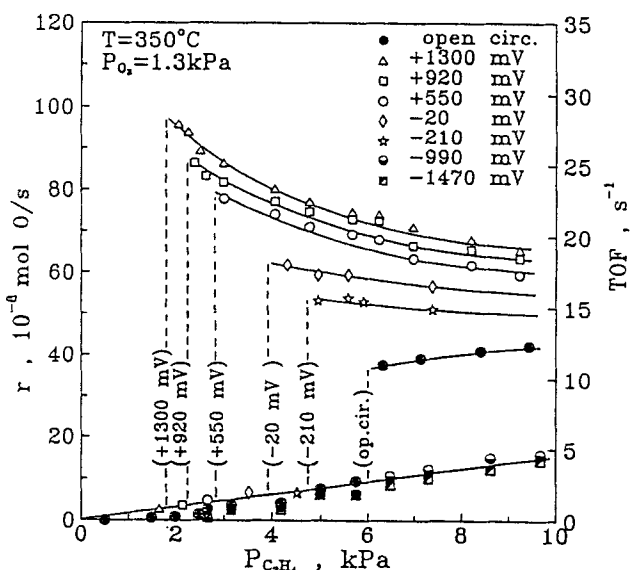

Fig. 3. Effect of $P_{C_2H_4}$ and catalyst potential on the rate of C_2H_4 oxidation on Rh.

change of catalytic activity is due to the formation of Rh oxide [25].

Figure 2 shows the effect of P_{O_2} and catalyst potential on the reaction rates. For low P_{O_2} values (reduced surface, $P_{O_2} < P_{O_2}^*$) increasing V_{WR} causes a significant, up to three-fold, increase in the reaction rate relative to its open-circuit value. The main feature, however, is the significant increase in P_{O_2} with increasing V_{WR} which causes a dramatic, up to hundredfold, increase in catalytic rate for intermediate P_{O_2} values. For higher P_{O_2} values there is practically no effect.

The same trend is presented in Fig. 3 which shows the effect of $P_{C_2H_4}$ and fixed catalyst potential on the rate of C_2H_4 oxidation. The low rate branch corresponds to an oxidized surface ($P_{C_2H_4} < P_{C_2H_4}^*$), while the high rate branch corresponds to a reduced surface.

It is worth noticing that the main feature of Figures 2 and 3 is the pronounced destabilization of surface Rh oxide with increasing catalyst potential which is the main cause of the observed dramatic rate enhancement.

3.2 NEMCA studies for the $C_3H_6/O_2/Pt$ system.

This reaction was studied at a temperature range between $380^{\circ}C$ and $480^{\circ}C$. By changing catalyst potential V_{WR} (with respect to a reference electrode) to more negative values, significant increase of the reaction rate, up to 600%, was observed. The enhancement factor Λ is in the order of -3×10^3. Application of positive potentials has no effect on the reaction rate. The kinetics of the reaction were investigated by varying the partial pressures of the components and catalyst potential V_{WR}.

Figure 4 shows the effect of $P_{C_3H_6}$ and catalyst potential on the reaction rate. The appearance of a sharp maximum at relatively low $P_{C_3H_6} \approx 0.2$ kPa indicates that the reaction exhibits a Langmuir-Hinshelwood kinetic behavior. Application of a large negative potential (-2000 mV) has a small effect on the reaction rate only on the fuel-rich region where the rate is independent from the $P_{C_3H_6}$.

Figure 5 shows the corresponding effect of P_{O_2} and catalyst potential. A wide maximum is noticed at relatively high P_{O_2}. Application of a negative potential equal to -1800 mV has a significant effect on the reaction rate only on the oxygen-lean region.

We conclude that propylene oxidation reaction on Pt exhibits a typical Langmuir-Hinshelwood kinetic behavior where propylene adsorption is stronger. This is the main reason why this reaction exhibits only electrophilic NEMCA behavior. Application of negative potential
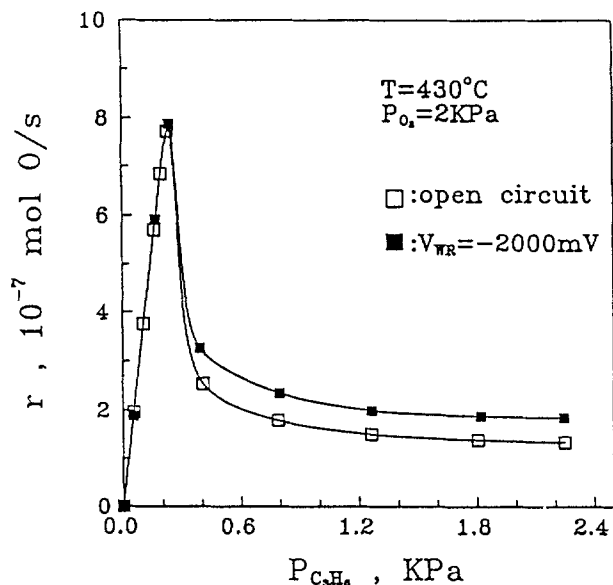
Fig. 4. Effect of $P_{C_3H_6}$ and catalyst potential on the rate of C_3H_6 oxidation on Pt.

Fig. 6. NEMCA induced compensation effect during C_2H_4 oxidation on Rh: Arrhenius plots at fixed V_{WR} values.

results to a strengthening of Pt-O bond, as oxygen is electron acceptor, and to a weakening of Pt-C_3H_6 bond, since propylene is electron donor. Figure 5 shows that electrophilic NEMCA is obtained only in the region where the reaction rate strongly depends from P_{O_2} (oxygen-lean-conditions). This happens because oxygen adsorbs more strongly on the surface and reacts faster with adsorbed propylene which becomes more weakly bound on the surface. When the coverage of oxygen becomes comparable with the coverage of propylene (oxygen-rich conditions) the effect is diminished. This is
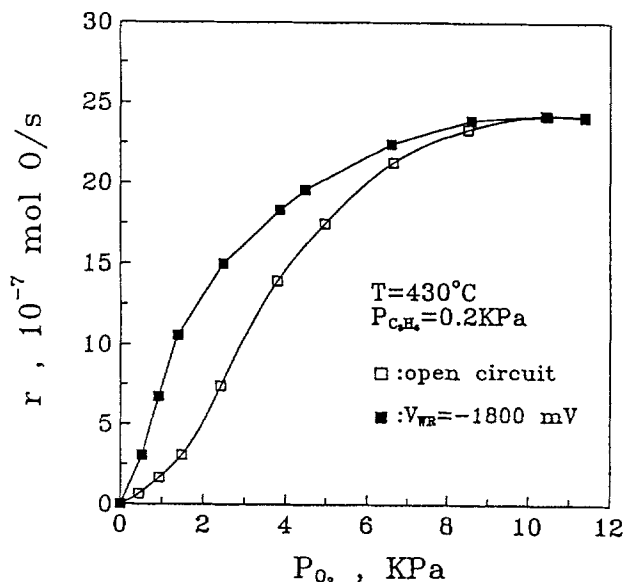

Fig. 5. Effect of P_{O_2} and catalyst potential on the rate of C_3H_6 oxidation on Pt.
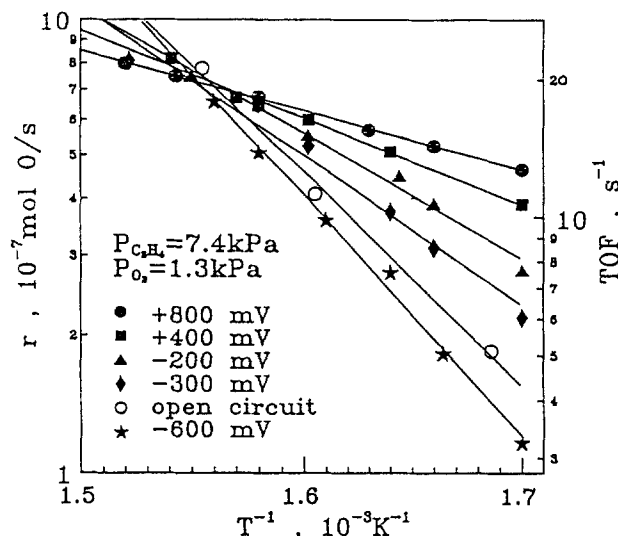
confirmed on Figure 4 where electrophilic NEMCA is exhibited only on the fuel-rich region but the effect is smaller as the propylene coverage is much larger than the oxygen coverage. Application of positive potential has no effect on the reaction rate due to the much stronger adsorption of propylene.

3.3. *Effect of V_{WR} and work function on activation energy. Compensation effect.*

Figures 6 and 7 show Arrhenius plots obtained at fixed V_{WR} values for the case of C_2H_4 and C_3H_6 oxidation, respectively. Figure 6 shows that by increasing V_{WR}, a dramatic decrease in activation energy is caused with a concomitant decrease in the preexponential factor r^o defined from

$$r = r^o \exp(-E/RT) \qquad (3)$$

As a result of this, Fig. 6 presents a striking demonstration of the compensation effect with an isokinetic point at $T_\Theta = 372^\circ C$.

It is worth noting that below the isokinetic point $(T < T_\Theta)$ the reaction exhibits electrophobic behavior i.e., $\partial r / \partial V_{WR} > 0$ and thus $\alpha > 0$ and $\Lambda > 0$, while above the isokinetic point $(T > T_\Theta)$ the reaction exhibits electrophilic behaviour i.e., $\partial r / \partial V_{WR} < 0$ and thus $\alpha < 0$ and $\Lambda < 0$. At $T = T_\Theta$ the NEMCA effect disappears.

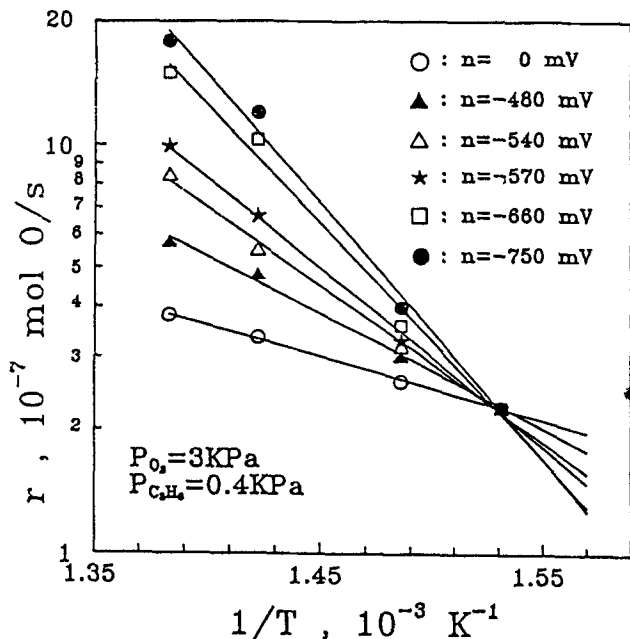The opposite behavior is presented in Figure 7, refering to C_3H_6 oxidation. In this case by decreasing the

Fig. 7. NEMCA induced compensation effect during C_3H_6 oxidation on Pt: Arrhenius plots at fixed V_{WR} values.

V_{WR} to more negative values, the activation energy and concomitantly the preexponential factor are increasing. In this figure the isokinetic point is observed at $T_\Theta=380^\circ C$. The reaction exhibits electrophilic behaviour in the temperature range of the investigation, while below the isokinetic point ($T<T_\Theta$) electrophobic behaviour should be expected. This figure also indicates that the NEMCA effect vanishes at the isokinetic point.

4. Conclusions

It was found that ethylene oxidation on Pt exhibit a pronounced NEMCA behavior. In the case of ethylene oxidation we measured the highest rate enhancement ratio observed so far (~ 100). It was also shown that the catalytic rate and also the location of the abrupt rate transition, corresponding to the formation of a surface oxide, can be adjusted by means of the externally applied potential.

In the case of propylene oxidation strong Non-Faradaic behavior was observed upon applying negative potentials and thus, removing O^{2-} from the catalyst surface.

The former reaction exhibit electrophobic behavior while the latter electrophilic behaviour. Both reactions exhibit a well defined compensation effect with the iso-

kinetic point lying within the temperature range of the investigation.

5. References

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