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The role of sodium surface species on electrochemical promotion of catalysis in a Pt/YSZ system: The case of ethylene oxidation

Naimah Ibrahim^{1,2}, Danai Poulidi^{1,†} and Ian S. Metcalfe^{1*}

¹*School of Chemical Engineering and Advanced Materials, Newcastle University,
Merz Court, Newcastle upon Tyne, UK, NE1 7RU*

²*School of Environmental Engineering, Universiti Malaysia Perlis,
02600 Arau, Perlis, Malaysia*

*i.metcalfe@newcastle.ac.uk

Abstract

The role of sodium addition as foreign (impurity) species on the electrochemical promotion of ethylene oxidation in a Pt/YSZ system was investigated. It was found that the presence of sodium surface species on the catalyst surface can significantly affect its catalytic and electrocatalytic properties, but there is no clear evidence at this stage that such species are necessary for the observation of EPOC. Under negative polarisation, low coverage sodium was found to have a pronounced effect on the electrochemical promotion of ethylene oxidation as an electronic promoter. The reaction changed behaviour from electrophilic at low sodium coverage (0.11%) and low to intermediate oxygen partial pressure ($p_{O_2} \leq 3.0$ kPa) to electrophobic at high sodium coverage (65%) and under high oxygen partial pressures ($p_{O_2} = 8.0$ kPa). In between the two sets of conditions, the reaction showed volcano-type behaviour depending on the coverage of sodium and gas phase oxygen partial pressure.

Keywords

EPOC, Surface impurities, Sodium promotion, Platinum, Ethylene oxidation

† Current address: School of Chemistry and Chemical Engineering, Queen's University
Belfast, David Keir Bld, Stranmillis Rd, Belfast BT9 5AG, UK

1. Introduction

Catalyst promoters are very often used in heterogeneous catalysis as the means to improve catalyst performance by enhancing the activity or changing the selectivity of a catalyst. Promoters can be supplied to the catalyst either during preparation (*ex situ*) or *in situ* via some form of catalyst-support interaction [1]. Electronic promoters (i.e. promoters that affect the catalyst performance by changing the chemisorptive bond properties of the reactants and reaction intermediates) have attracted a lot of attention in the past three decades, especially in the area of Electrochemical Promotion of Catalysis (EPOC). EPOC studies the effect that the *in situ* supply of promoting species via the application of an external electrical (or chemical) overpotential between a metallic catalyst/electrode (supported on an ionic conducting membrane) and a counter electrode has on the catalyst performance [2-3]. It has been found [3-4] that the origin of EPOC lies in the backspillover (from the support to the catalyst) of ionic promoting species that form (together with their mirror charge) an overall neutral double layer on the catalyst surface thus changing the work function of the catalyst and modifying its activity and selectivity. EPOC has been studied for a wide range of reactions [5-8], catalysts [9-12] and different ionic conducting supports such as oxygen ion [12-13], protonic [14-15] and alkali ion conductors [7, 16-18]. The promoting species (that originate from the support) depend on the choice of catalyst support (i.e. oxygen ions for an oxygen ion conductor etc.).

While extensive studies exist to predict and investigate the behaviour of catalytic systems under controlled spillover (EPOC) conditions, where the supply of promoting species is dictated by the imposed electrical overpotential or current, very little work has been carried

out to investigate the effect of pre-existing species (that can be found on the catalyst surface in the form of uncharacterised impurities) such as metal cations. Such species may have promoting properties and are often (as in the case of alkali metals) used as additives during catalyst preparation in order to enhance the catalytic activity [19]. In other cases pre-existing impurities (such as silicon) may block the catalyst active sites thus poisoning the catalyst [20]. In fact, the question whether pre-existing impurities on the catalyst surface may be responsible for the observed rate modification in EPOC, via some interaction with the spillover species (oxygen or other) has not been successfully addressed to date.

In this work we will investigate the role of sodium addition to a platinum catalyst-film interfaced with an yttria-stabilised-zirconia (YSZ) dense electrolyte membrane under catalytic (open-circuit) and electropromoted (polarised) conditions. Ethylene oxidation will be used as the probe reaction. Sodium is chosen in this study due to the promoting properties it has been found to have in heterogeneous catalysis [21-25]. This study aims to study the combined effect of *ex situ* (sodium) and *in situ* (electrochemically supplied oxygen ions) promoters in order to assess the possible interactions between them and their combined effect on promotion. To that effect samples with sodium surface coverage from 0.11-65% have been used in this work. We must of course stress that we should not (and in fact do not in this work) treat surface species of coverage higher than 10% as impurities as such coverages would be expected to have very pronounced effects even on the nature of the catalyst. It is however, important for our work to study a wide range of sodium surface coverage in order to obtain a more complete picture of the role of sodium in the catalytic and electropromoted behaviour of the catalyst.

In heterogeneous catalysis and surface science, alkali metals such as sodium are known to affect the activity of a metal catalyst and the use of alkali metals as catalyst promoters has been well-documented [26-29]. For example, a study by Bertolini et al showed that the

coverage of the alkali metal affects the adsorption of gases (in the case of their study oxygen and carbon monoxide) on the catalyst surface [28]. The study showed that at low coverage, the alkali metal was mostly in ionic form and could induce large modification to the electronic properties of the neighbouring platinum surface atoms, causing an increase in the adsorption of an electron acceptor like CO on the catalyst surface. In contrast, at high coverage, the alkali metal was mostly in metallic form and had a great affinity for oxygen thus enhancing oxygen adsorption. The effect of sodium on the activity of a metal catalyst may also be viewed as a change in the catalyst work function [26, 30-31]. Some of the electronic charge of the sodium atoms can be transferred to e.g. the platinum metal because the ionisation energy of a sodium atom (5.1 eV) is lower than the work function of platinum (5.9 eV) [30]. The charge forms dipoles at the surface resulting in a lower platinum work function. We can see therefore that there may be an analogous effect between the sodium addition- and polarisation-induced work function changes with respect to the observed rate modification on the catalyst system. In EPOC, sodium has been successfully used as a promoter via the use of sodium ion conducting supports such as β'' -Al₂O₃ [16, 32-33] and Na₃Zr₂SiPO₁₂ (NASICON) [17-18, 34].

Ethylene oxidation over platinum is a well-studied probe reaction for EPOC. In the case of ethylene oxidation, the promotional behaviour of the system has been found to be dependent upon the gas-phase composition and on the ratio between the partial pressure of oxygen over partial pressure of ethylene [35].

2. Model of promotion

Next, we will propose a model that will help us evaluate the role of sodium addition on the catalytic and electropromoted properties of the Pt/YSZ system. As discussed earlier, sodium

may affect a catalytic reaction in a number of ways, such as by causing a change in the work function of the catalyst (a long range effect) or by modifying the activity of catalyst sites in the vicinity of the sodium species (short range effect). Moreover, sodium species may directly interact with the gas phase reactants by creating different reaction intermediates and pathways that can affect the catalytic reaction rate. When studying the electropromoted behaviour of a catalyst system, the addition of another type of promoter (oxygen ions in the case studied here) leads to a complex system where possible interaction not only between each promoting species and the reaction components (i.e. catalyst, reactants and intermediates) but also between the two types of promoters could influence the behaviour of the reaction. A complex model would be required in order to fully predict and explain the behaviour of such a system. In this work we will, in the first instance, test a very simple model by making certain assumptions about the interactions between all of the species. We will initially disregard any short range effects caused by sodium addition and also any interaction between the sodium and oxygen promoting species. We would anticipate this assumption to be valid at low promoter coverage (both sodium and oxygen ions). Under these assumptions we would expect equal work function changes to cause equal rate modification regardless of the origin of the work function change (i.e. sodium addition ex situ or oxygen spillover in situ by electrical polarisation) and that the total rate change observed as a result of the combined promotion by sodium and oxygen species could be predicted by the total catalyst work function change.

Based on this model we would expect that sodium addition and negative polarisation (i.e. removal of oxygen ion species from the catalyst surface) to have a qualitatively similar effect on the catalytic reaction rate as they both lower the work function of the catalyst. The effect of promotion would depend upon the behaviour of the reaction, i.e. electrophilic, electrophobic, volcano or inverted volcano. According to Vayenas's reaction classification

[8] for an electrophilic reaction the rate decreases as the work function of the catalyst increases, while for an electrophobic reaction the rate increases for increasing work function i.e.:

$$\partial r / \partial \Phi < 0 \quad (1)$$

$$\partial r / \partial \Phi > 0 \quad (2)$$

A reaction exhibiting volcano-type behaviour has a rate maximum at $U_{WR} = 0$ while a reaction with inverted volcano behaviour shows a rate minimum at $U_{WR} = 0$, where U_{WR} is the potential between the working and reference electrodes.

For an electrophilic reaction we would see a rate increase caused by sodium addition and negative polarisation and a rate decrease caused by positive polarisation (i.e. supply of oxygen ions to the catalyst) and vice versa for an electrophobic reaction; the combined effect of sodium addition and positive polarisation would be harder to predict as the total work function change could be positive or negative depending on the sodium coverage and applied potential. For inverted volcano behaviour we would expect to observe a rate increase for any perturbation of the work function of the catalyst (sodium addition or oxygen spillover) and the opposite is expected for reactions with volcano-type behaviour.

3. Experimental

An experimental rig was constructed using stainless steel Swagelok compression fittings and Perfluoroalkoxy (PFA) tubing as described in [36]. The flow of gas to the electrochemical reactor was controlled by electronic mass flow controllers (MFCs) provided by Chell Hastings. The gases used here were 20% O_2/He , 10% C_2H_4/He and CP grade He (N5) provided by BOC with typical flowrates of 200 ml (STP) min^{-1} . The flowrates of the

gases were also measured at the outlet using a Varian digital flowmeter (1000 series). The single chamber electrochemical reactor and three-electrode pellet system used in the study have already been described in detail in our previous work [36]. The solid electrolyte disc of 20 mm diameter and 2 mm thickness was prepared by uniaxial pressing at approximately 1 ton cm⁻² of 2.2 g of 8 mol% YSZ powder provided by Pi-Kem Ltd, UK and sintered at 1500 °C for 12 hours. After shrinkage during sintering the resulting pellet had a diameter of 15 mm and a thickness of 1.5 mm. On one side of the disc a platinum catalyst film (Metalor) was deposited as the working electrode, while on the other side two gold films (Metalor A1118) that served as the counter and reference electrodes were deposited. The resulting working and counter electrodes were each calculated to have a geometric projected surface area, A , of approximately 0.88 cm². The electrochemical measurements were conducted using an Ivium Compactstat, while the gases were analysed using a BINOS CO₂ analyser and a Varian gas chromatograph.

Sodium was deposited dropwise using 1 µL of sodium hydroxide (NaOH) solutions (Alfa Aesar) on the platinum surface using a fixed micropipette followed by drying in air at 400°C for one hour. Table 1 summarises the sodium loading (per platinum surface area) and the percentage of nominal sodium coverage. Details of the sodium deposition method and the calculation of sodium loading/coverage are as reported in our previous work [37]. Unless otherwise stated the sodium loadings reported in Table 1 are cumulative. The samples are named as Sample xyy , where x and yy denotes the most recent concentration of the NaOH solution deposited on the platinum surface (NaOH concentration = $x \cdot 10^{-yy}$ M). Kinetic studies were carried out on Sample A (which was then subsequently added with NaOH solution from 10⁻⁴ to 5x10⁻²M, resulting in Samples A104 to A502) under open and closed circuit conditions at 350°C. Ethylene partial pressure was kept constant at 0.5 kPa for all the experiments reported here while the oxygen partial pressure was varied between 0.5 and 8

kPa. The reaction rates reported here are expressed in terms of moles of CO₂ produced per unit area per unit time (where the area used for the rate calculations is the geometric projected surface area of the catalyst/electrode) and are calculated based on the outlet composition of the reactor. In the figures where discrete data points for reaction rates are used, error bars of 5% are included in the plots. This accounts for inaccuracies in the measurement of the CO₂ partial pressure and the total volumetric flow rate at the outlet of the reactor and possible fluctuations of the electronic mass flow controllers used to deliver the flow of gases to the reactor. We believe this to be a good estimate, based on the manufactures specification for the instruments used and the fact that during repeat experiments under similar conditions the calculated reaction rates did not differ by more than 5%. In addition the discrete rate data points represent average values taken from transient experiment; these averages were taken when the rate was assumed to have reached steady state, for the purpose of our work this meant that the rate variation was less than 5%. When reporting transient rate data no error bars are used in the figures.

Two commonly used parameters to express the magnitude of promotion [3], i.e. rate enhancement ratios, ρ , and faradaic efficiencies, Λ will be employed in discussing the effect of sodium addition to EPOC:

$$\rho = r/r_o \quad (3)$$

$$\Lambda = \Delta r/(i/2F) \quad (4)$$

where r is the electropromoted catalytic rate, r_o is the unpromoted (open-circuit) catalytic rate, Δr is the difference on the reaction rate between polarised and open-circuit conditions, i is the applied current density and F is the Faraday's constant. In addition, under open-circuit conditions where the modification of the catalytic rate is only caused by sodium (and not the applied overpotential), the rate enhancement ratio, ρ_{Na} , is defined as the ratio of the sodium-

modified sample reaction rate (r_{Na}) over the rate of the ‘clean’ sample (r_{clean}), both measured under open-circuit conditions:

$$\rho_{\text{Na}} = r_{\text{Na}}/r_{\text{clean}} \quad (5)$$

Scanning electron microscopy (SEM), JEOL 5300’s scanning electron microscope (SEM) fitted with energy-dispersive X-ray (EDX) light element analysers was used in order to obtain pre- and post-operation images of the catalyst film and to investigate the presence of elements on fresh and used sodium-modified samples. Note that the EDX measures the presence of elements to a depth of several micrometers into the sample surface. Therefore the EDX results could not be used to quantify the elemental constituents on the platinum surface, rather for simple identification and distribution mapping of significant elements such as platinum and sodium. SEM analysis of the ‘clean’ and sodium-modified samples has been presented in our previous work [36].

X-ray Photoelectron Spectroscopy (XPS) measurements were also carried out to study the chemical state and composition of the catalyst surface. The samples (B000-J101) used for the XPS measurements were eight fresh platinum films made from Heraeus platinum paste and supported on YSZ solid electrolyte, seven of which were impregnated with variable concentration of NaOH solutions (ranging from 10^{-12} to 10^{-1} M) following the same sodium deposition method as for the samples used for kinetic experiments. The XPS measurements were performed using a Thermo K-Alpha electron spectrometer with a monochromated Al $K\alpha$ X-ray source (1486.6 eV, $1 \text{ eV} = 1.6302 \times 10^{-19} \text{ J}$) with a spot size of approximately 400 μm on the sample surface. The instrument has a hemi-spherical electron energy analyser; survey spectra were taken at a pass energy of 200 eV and narrowscan spectra around the principal peaks of the elements present (i.e. C, O, Na, Pt, Zr and Y) with a pass energy of 50 eV. The narrowscan spectra were taken from four points in a line for each of the 8 samples.

These points on each line were about 2.5 mm apart, and shown in Fig. 1. For each line scan, the first three points were on the platinum region, and the last point was on the YSZ region. The base pressure in the analysis chamber was kept below 1×10^{-8} mbar during data acquisition. The pass energy of the analyser was set at 50 eV for the narrowscans, for which the resolution as measured by the full width at half maximum (FWHM) of the Ag 3d_{5/2} peak was 0.85 eV. The binding energies were referenced to Au using the manufacturer's automatic calibration software.

4. Results and discussion

4.1 XPS Analysis

The surface of a nominally 'clean' Pt/YSZ catalyst system (Sample B000) and the Na-modified samples (C112-J101) were characterised using XPS (these were all fresh samples and were not used in kinetic experiments). Typical O 1s, Na 1s, C 1s, and Pt 4f spectra are shown in Fig. 2 (only those obtained from Point 3 in Fig. 1 are shown). Similar spectra with respect to the peaks of O 1s, Na 1s, C 1s, and Pt 4f were obtained for all other points in the platinum regions, except for some shifts in the binding energies, and changes in the peak intensities probably due to non-homogeneity in sodium distribution on the catalyst surface.

The nominally 'clean' sample in Fig. 2a exhibited two main O 1s components at binding energies of 530.2 and 532.2 eV. The former indicates the presence of lattice oxygen, this signal belongs to the oxidic contribution of the YSZ [38], and the latter indicates the existence of oxygen from other groups such as hydroxides, carbonates and/or oxides on the surface of the platinum films [39-41]. Increasing the sodium coverage on the catalyst surface masks the O 1s signal arising from the solid electrolyte (the first peak), while at the same time increases the second peak suggesting that this peak may be associated with sodium. As

can be seen from Fig. 2b, a broad peak for Na 1s can be seen for the ‘clean’ sample, as well as for the samples of low sodium coverage (below 1%). This broad peak, (which could represent more than one chemical states of sodium on the catalyst platinum surface, such as sodium carbonates, sodium oxides or hydroxides), becomes sharper and larger as the sodium coverage increases. For Samples H502 and J101 the binding energy of Na 1s peaks at 1071.5 eV indicating the presence of sodium carbonates on the platinum surface [42]. This can be further confirmed from the C 1s spectra (shown in Fig. 2c) that also indicate the presence of carbonates (binding energy 289.2 ± 0.2 eV) for Samples H502 and J101 [42]. The C 1s peak at binding energies above 284 eV is normally assigned to graphitic carbon species that may originate from impurities on the catalyst surface due to sample preparation and handling. The binding energy of Pt 4f_{7/2} at 70.8 ± 0.3 eV in Fig. 2d indicates that the platinum catalyst on all samples is in metallic form [41]. This suggests that sodium addition has not significantly modified the chemical state of the platinum catalyst¹.

The intensity of the Na 1s peaks for all samples at the four different acquisition points is plotted against the nominal % sodium coverage in Fig. 3. An increase in sodium coverage increases the Na 1s intensity. It appears that sodium is non-uniformly distributed on each acquisition point (the highest scatter is observed for the sample with the highest sodium coverage). The presence of sodium on Point 4 could be due to the mobility of sodium and sodium impurities pre-existing on the YSZ electrolyte; the manufacturer reports that the YSZ powder contains approximately 100 ppm Na₂O). As we can see from Fig. 3 the ‘clean’ sample (B000) has similar Na 1s peak intensity to the samples with coverage less than 1% (Samples C112 to E104). This could possibly be due to impurities pre-existing on the platinum surface and / or the de-ionised water used to prepare the NaOH solutions (pre-

¹ In Point 1 of some samples (spectra not shown), there is an indication of the existence of platinum hydroxide species at 72.3 ± 0.3 eV [NIST X-ray Photoelectron Spectroscopy Database 2000, National Institute of Standards and Technology (NIST), <http://srdata.nist.gov/xps/>, Accessed on 12 November 2012.].

existing impurities will be more significant for solutions of low NaOH concentration and thus for samples of low coverage).

4.2 Kinetic studies

Next we will discuss the results obtained from the kinetic experiments performed on ‘clean’ and sodium-modified samples under open-circuit and polarised conditions.

4.2.1 *Open-circuit conditions*

Fig. 4 shows the CO₂ production rate of all samples under open-circuit conditions; while Table 2 lists the rate enhancement ratio caused by sodium addition, ρ_{Na} . As we can see from Fig. 4 the rate of CO₂ production is positive order with respect to oxygen partial pressure. This is true for all the samples (i.e. ‘clean’ and sodium-modified). This has also been consistently reported in the literature (e.g. [9]). From Fig. 4, we can see that sodium addition in general increases the open-circuit rate. This effect becomes more pronounced at high sodium coverage and for low oxygen partial pressure in the reaction mixture. Thus the highest enhancement ratios ($\rho_{\text{Na}} \approx 4$) are observed for 65% sodium coverage and oxygen partial pressures up to 1.5 kPa (stoichiometric oxygen to ethylene ratio). The results obtained under open-circuit conditions are, in the first instance, in qualitative agreement with the proposed model (for an electrophilic reaction), in the sense that in general sodium addition resulted in an increase of the reaction rate as predicted by the model. Of course, whether this promotion is simply due to the work function changes caused by sodium, or also caused by additional interaction between the sodium species and the reactants or the oxygen promoting species, cannot be assessed at the moment and will be discussed in more detail when the experiments under polarisation are discussed.

4.2.2 Polarised conditions

Figures 5 and 6 show the reaction rate transients during polarisation which lasts for seven minutes (420 s). The reaction rate is monitored for an additional five minutes prior to polarisation, and approximately 15 minutes after polarisation (in some cases the final open-circuit step is longer as the return to the initial open-circuit rate can be slower depending on the experimental conditions). In Figs. 5a-b we can see the transients for an oxygen partial pressure of 3.0 kPa (results for lower partial pressures are not shown but showed similar trends) while Figs. 6a-b show the behaviour under an oxygen partial pressure of 8.0 kPa (high p_{O_2}). For both Figs. 5 and 6, figure a corresponds to negative polarisation with an overpotential of -1 V and figure b corresponds to positive polarisation at an overpotential of 1 V. In addition, Table 3 shows the enhancement ratios and faradaic efficiencies observed under all experimental conditions studied here. As can be seen here the reaction shows in general electrophilic behaviour for sodium coverage less than 1% (Sample A104) and oxygen partial pressure up to 3.0 kPa (i.e. fuel rich to mildly fuel lean conditions) since application of a negative potential (Fig. 5a) leads to an increase of the reaction rate while positive potential causes a rate decrease (Fig. 5b). This has also been observed in our previous work [37]. The effect of sodium (at a low coverage) becomes less pronounced at high oxygen partial pressures (as seen in Fig. 6) where no significant rate modification is observed; in fact polarisation appears to simply stabilise the oscillating reaction rate for both the clean sample and the 0.11% coverage (the stable rate is slightly lower than the oscillatory rate observed prior to and after polarisation). However, as the sodium coverage increases, the effect of polarisation at high oxygen partial pressures becomes more pronounced. This indicates that under these conditions there may be an interaction between the sodium surface species and the oxygen both from the gas phase and from the oxygen ion supply (this interaction is expected at high sodium coverage as indicated in our model discussion earlier on). As shown

in Table 3 the reaction shows volcano-type behaviour for oxygen partial pressures of 8.0 kPa (at all sodium coverages) while the oxygen partial pressure where volcano behaviour is first observed decreases with increasing sodium coverage (so for a sodium coverage of 65% the reaction shows volcano-type behaviour even at sub-stoichiometric oxygen to ethylene ratios, $p_{O_2} = 0.5$ kPa). In addition for a sodium coverage of 65% and an oxygen partial pressure of 8.0 kPa the reaction becomes electrophobic as a rate enhancement is only observed under positive polarisation (Fig. 6b).

With respect to the polarisation experiments we can see from Figs. 5 and 6 that the observed currents under negative and positive polarisation show a different behaviour as a function of the sodium coverage. While under negative polarisation the observed current densities were very similar for all samples (around $-20\mu A\ cm^{-2}$) this was not the case under positive polarisations where, in general higher sodium coverages resulted to higher current densities (current densities varied from 20 - $150\mu A\ cm^{-2}$). A similar behaviour was observed during electrochemical measurements under non-reactive atmospheres (not shown here) where a limiting current density of approximately $20\mu A\ cm^{-2}$ had been observed for cathodic polarisation lower than $-0.5V$, while no limiting currents were observed for anodic polarisation in the range of overpotentials used. This suggests that sodium addition does not affect the rate of oxygen reduction taking place at the three phase boundary under cathodic polarisation. In contrast the supply of oxygen ions from the electrolyte to the three phase boundary and the catalyst surface is facilitated by sodium addition (as indicated by the increased currents observed). This may be related to e.g. the creation of sodium oxide or hydroxide species on the catalyst surface and may be linked to the changing behaviour of the reaction at high sodium coverage from electrophilic to volcano and electrophobic (for both high oxygen partial pressure and sodium coverage).

5. Discussion

The experimental data under varying sodium coverages and oxygen partial pressures exhibit the following key features:

- Increasing sodium coverage up to 65% appears to promote the open-circuit catalytic activity of the Pt/YSZ system for ethylene oxidation; the sodium-induced rate enhancement is reduced by an increase in the oxygen partial pressure
- The system exhibits electrophilic behaviour at low sodium coverage and under fuel-rich conditions to mildly fuel-lean conditions ($p_{\text{O}_2} = 0.5\text{-}3.0$ kPa), however this promotional behaviour appears to be changed to volcano and finally electrophobic by increasing oxygen partial pressure and sodium coverage

We will now test the work function dependent model proposed earlier on with the experimental data obtained in this work. We will initially consider the case of low oxygen partial pressures where the reaction showed electrophilic behaviour; this is shown in Fig. 7. In order to test our model we must first estimate the work function changes of the platinum film caused by sodium addition. In our previous work [36] we had measured via the Kelvin Probe technique the work functions of several platinum films of different sodium coverage (namely ‘clean’, 0.11% and 11%). From these values we can calculate the work function changes between the clean and the sodium-modified samples. In order to calculate these changes we use the average work function of all the samples of the same sodium coverage (and also calculate the corresponding standard error) and find the difference between the average work function of the clean samples and the average work function corresponding to each sodium coverage (in addition the corresponding standard error of the difference is also calculated). Based on these calculations we obtained that the work function changes (with respect to the work function of a ‘clean’ sample) for samples of 0.11% and 11% sodium coverage were -100 ± 70 and -200 ± 80 meV respectively. We must, however,

note that these measurements were performed in air (at room temperature) and may as a result deviate from work function changes caused by sodium addition under operating conditions. The work function change caused by a sodium coverage of 65% was extrapolated from the measured values assuming a linear dependence between work function [3] and sodium coverage and is estimated to be -950 ± 100 meV (in this case the corresponding error was calculated by the errors of the linear extrapolation); it is possible that an even larger error may be associated with this estimation as work function changes may not in fact have a linear dependence on sodium coverage under the operating conditions. For the electrically induced work function changes we assume that $\Delta\Phi = e\Delta U_{\text{WR}}^2$ (we have not included any error bars associated with electrically induced work function changes). Fig. 7 shows the rate dependence on work function change for an oxygen partial pressure of 1.5 kPa. The three sets of data in the dotted boxes correspond to the nominally ‘clean’ sample (circle) and those modified with 10^{-4} M (0.11% Na coverage, triangle) and 10^{-2} M (11% Na coverage, star) NaOH solutions (for open-circuit, positive and negative polarisation). As we can observe in the figure, in general the reaction rate changes at low sodium coverage (0.11%) follow the proposed work-function dependent behaviour for an electrophilic reaction, where negative polarisation generally enhances the reaction rate due to a decrease in the catalyst work function, while positive polarisation reduces the reaction rate as it increases the catalyst work function. Sodium addition enhances the rate increase caused by negative polarisation and reduces the rate decrease for positive polarisation.

While we can comment on a qualitative agreement between the proposed model and the experimental data, we also notice that a deviation from the model exists; this suggests a possible interaction between either the two promoting species or between the promoters and

² In EPOC studies the change in the work function of a catalyst due to electrical polarisation ($\Delta\Phi_{\text{el}}$) is linked to the applied potential between the working and the reference electrode (U_{WR}) or overpotential via the relation: $\Delta\Phi_{\text{el}} = \xi e\Delta U_{\text{WR}}$, where ξ depends on operating conditions and electrode morphology [I.S. Metcalfe, Journal of Catalysis, 199 (2001) 247-258].

the reactants or intermediates. In particular, we can observe that while a sodium coverage of 0.11% does not significantly change the reaction rate it induces a much higher electropromoted rate at negative polarisation than that of a 'clean' pellet indicating an interaction between the oxygen and sodium promoting species. The total rate increase for the sodium-modified electropromoted sample is not therefore equal to the addition of the rate changes from sodium addition and polarisation alone. This can be seen in Figs. 5a and 7. Moreover, as discussed earlier on and is also shown in Fig. 7 at high sodium coverage the reaction changes behaviour to volcano-type and the rate data deviate significantly from the model. These observations suggest that the two promoting species interact with each other thus creating a more complex response of the system than the one anticipated by the proposed model.

Next, we will further discuss the role of sodium on the changing behaviour of the reaction under EPOC conditions. As mentioned earlier the reaction behaviour changes with increasing oxygen partial pressure and sodium coverage from electrophilic, to volcano and finally to electrophobic. This is shown schematically in Fig. 8a while Fig. 8b illustrates this shifting behaviour with experimental data. Under polarisation, the electrophilic behaviour observed at low sodium coverage and under low oxygen partial pressure can simply be explained by stronger ethylene (electron donor reactant) adsorption in comparison to oxygen (electron acceptor reactant) in accordance to the more ionic character sodium exhibits at low coverage. An increase in sodium coverage (and also gas phase oxygen) however may result in an increase in oxygen adsorption, and possibly also modify the competitive adsorption between oxygen and ethylene, as sodium becomes more metallic [28]. In the intermediate region of sodium coverage and oxygen partial pressure volcano behaviour should then be observed (where both reactants are strongly adsorbed), while at high sodium coverage, when eventually the oxygen becomes more strongly adsorbed than the ethylene, the electrophobic

behaviour can occur. This change in the apparent behaviour of the reaction, which appears to be caused primarily by the sodium addition, is in fact a manifestation of the complexity of the interaction between all the species of this catalytic system. The interaction between the two promoting species could be used to explain some of the differences in experimental results presented by different research groups on nominally similar catalyst systems where the raw materials are often obtained from different sources. As an example, while most studies conducted on the electrochemical promotion of ethylene oxidation on Pt/YSZ show that the reaction exhibits electrophobic behaviour for a wide range of conditions [42-43] in our work the reaction showed clear electrophilic behaviour for a nominally clean pellet; this may simply be due to the presence of different impurities on the raw materials used for the preparation of the different samples. This suggests that while surface species may not be necessary for the occurrence of EPOC they can significantly affect the behaviour of the system.

6. Conclusions

The study presented here showed that the presence of foreign surface species on a catalyst can significantly affect its catalytic and electrocatalytic properties. We cannot however, based on the evidence obtained from this work assess the necessity of such surface species for the occurrence of EPOC. In the case of sodium addition onto a platinum catalyst the observed behavioural changes have been partially explained by a model that considers work function changes caused by each promoter species independently. The model can, for low sodium coverage predict an additive effect between sodium addition and polarisation. However, experimental results indicated that the two promoter species are not completely independent of each other especially at high sodium coverage. With increasing sodium coverage the

reaction behaviour changes from electrophilic to volcano-type (possible to an increase in the chemisorptive bond strength of oxygen on the platinum catalyst), while for high sodium coverage, where the sodium is known to adopt a more metallic character, interaction with oxygen becomes more significant and the reaction shows electrophobic behaviour.

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Table/figure captions

Tables

Table 1. Estimation of sodium loading on platinum catalyst and percentage of sodium coverage. Sample A is used for kinetic studies and Samples B-J are used for XPS analysis.

Table 2. Rate enhancement ratios caused by sodium modification.

Table 3: Rate enhancement ratios and Faradaic efficiencies of all samples.

Figures

Fig. 1. Schematic drawing of the four acquisition points on each sample during XPS measurements.

Fig. 2. XPS spectra of nominally 'clean' and Na-modified Pt/YSZ catalyst systems.

Fig. 3. Relative intensity of sodium and platinum from XPS measurement versus nominal % sodium coverage.

Fig. 4. Open-circuit rates at varying oxygen partial pressures. Reactant partial pressures, variable p_{O_2} = 0.5, 1.5, 3.0 or 8.0 kPa, $p_{C_2H_4}$ = 0.5 kPa; Temperature = 350°C; Total flow rate = 200 ml min⁻¹.

Fig. 5: Transient plots under intermediate oxygen partial pressure and polarised conditions: (a) η = -1 V; (b) η = +1 V. Top: Current density, i versus time; Bottom: CO₂ versus time. Reactant partial pressures, p_{O_2} = 3.0 kPa, $p_{C_2H_4}$ = 0.5 kPa; Temperature = 350°C; Total flow rate = 200 ml min⁻¹.

Fig. 6. Transient plots under high oxygen partial pressure and polarised conditions: (a) η = -1 V; (b) η = +1 V. Top: Current density, i versus time; Bottom: CO₂ rate versus time. Reactant partial pressures, p_{O_2} = 8.0 kPa, $p_{C_2H_4}$ = 0.5 kPa; Temperature = 350°C. Total flow rate = 200 ml min⁻¹.

Fig. 7. CO₂ production rate under stoichiometric conditions as a function of work function changes (work function changes for sodium coverage of 0.11% and 11% were calculated from work function measurements performed in air; the work function change corresponding to 65% coverage is estimated by linear extrapolation from the measured values). Reactant partial pressures, $p_{\text{O}_2} = 1.5$ kPa, $p_{\text{C}_2\text{H}_4} = 0.5$ kPa; Temperature = 350°C. Total flow rate = 200 ml min⁻¹.

Figs. 8. Schematic representation (a) and actual example (b) of the rate changes with positive and negative polarisations as a function of sodium coverage and oxygen partial pressure

Table 1

Sample [†]	Volume NaOH μL	NaOH concentration M	Na atom	Na/Pt surface area atom cm^{-2}	% Na coverage
A000	Nominally 'clean' sample				
A104	1.00 ± 0.25	1×10^{-04}	6.0×10^{13}	1.1×10^{12}	0.11
A102		1×10^{-02}	6.1×10^{15}	1.1×10^{14}	11
A502		5×10^{-02}	3.6×10^{16}	6.5×10^{14}	65
B000	Nominally 'clean' sample				
C112	1.00 ± 0.25	1×10^{-12}	$6.0 \times 10^{05} \ddagger$	1.1×10^{04}	1.1×10^{-9}
D108		1×10^{-08}	$6.0 \times 10^{09} \ddagger$	1.1×10^{08}	1.1×10^{-5}
E104		1×10^{-04}	$6.0 \times 10^{13} \ddagger$	1.1×10^{12}	0.11
F103		1×10^{-03}	$6.0 \times 10^{14} \ddagger$	1.1×10^{13}	1.1
G102		1×10^{-02}	$6.0 \times 10^{15} \ddagger$	1.1×10^{14}	11
H502		5×10^{-02}	$3.0 \times 10^{16} \ddagger$	5.4×10^{14}	54
J101		1×10^{-01}	$6.0 \times 10^{16} \ddagger$	1.1×10^{15}	110

[†]Sample x_{yy} ; the most recent NaOH concentration = $x \times 10^{-yy}$ M

[‡]Not cumulative

Table 2

Sodium enhancement

p_{O_2} kPa	Rate enhancement ratio, ρ_{Na}		
	A104	A102	A502
0.5	0.58	1.29	3.96
1.5	1.04	1.90	3.81
3.0	0.90	1.90	1.82
8.0	1.06	0.87	1.27

Table 3

Negative polarisation

p_{O_2} kPa	Rate enhancement ratio, ρ				Faradaic efficiency, Λ			
	A000	A104	A102	A502	A000	A104	A102	A502
0.5	1.35	2.23	1.30	1.01	-138	-505	-299	-55.2
1.5	1.27	2.03	1.32	0.83	-177	-871	-724	322
3.0	1.28	1.84	0.88	0.76	-330	-1323	336	473
8.0	1.00	0.94	0.83	0.75	-2.12	172	666	1170

Positive polarisation

p_{O_2} kPa	Rate enhancement ratio, ρ				Faradaic efficiency, Λ			
	A000	A104	A102	A502	A000	A104	A102	A502
0.5	1.02	0.94	1.10	0.85	8.37	-65.7	29.5	-108
1.5	0.89	0.89	0.89	0.79	-148	-33.3	-84.9	-104
3.0	0.82	0.85	0.72	1.00	-1142	-157	-169	1.93
8.0	0.80	0.81	0.92	1.12	-1015	-283	-45.6	347

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5a

Fig. 5b

Fig. 6a

Fig. 6b

Fig. 7

8a.

8b.

Fig. 8