Electrochemical promotion of ethanol partial oxidation and reforming reactions for hydrogen production

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Abstract

The electrochemical activation of a Pt-KβAl$_2$O$_3$ catalytic system is studied for hydrogen production from ethanol. The in-situ intercalation of potassium ions onto the catalyst surface under negative polarization leads to hydrogen activation and an increase in the production rate under all explored conditions, observing a reproducible, controllable and reversible effect. Under ethanol partial oxidation conditions, the ions migration promotes oxidation dehydrogenation route vs. ethanol dehydration one. Moreover, the steam addition is evaluated through different reaction conditions: steam reforming, partial oxidation and autothermal reforming. The steam reforming reaction exhibits the highest initial catalytic activity; although a strong deactivation of the catalyst occurs due to carbonaceous species deposition. Comparing partial oxidation and autothermal reforming, the latter one presents the highest catalytic activity and the strongest electrochemical activation effect. These findings contribute to the Electrochemical Promotion of Catalysis phenomenon application to operando tuning the catalyst conversion towards hydrogen production, therefore expanding its application to hydrogen technology.

Keywords: electrochemical promotion, ethanol partial oxidation, hydrogen production, ethanol autothermal reforming, ethanol steam reforming

1. Introduction

Hydrogen nexus is a corner stone for a sustainable energy future to address both ever-growing energy demand and minimizing greenhouse gas (GHG) emission [1]. Hydrogen is as an excellent alternative to conventional fuels, because it has the highest specific energy among fossil fuels [2], and its production from biomass derived feedstocks like alcohols could contribute to lowering GHG emission [3].

Bio-ethanol has an industrial potential as the feedstock for hydrogen generation via low carbon processes, thanks to its easy storage, lower volatility, high hydrogen content per mole, absence of toxicity, abundance of biomass feedstocks as well as safe transport and handling [4,5]. Various processes exist for ethanol conversion to hydrogen such as aqueous phase reforming, dry reforming, steam reforming (SR), partial oxidation (POX), and autothermal reforming (ATR) [3,6–8], being the last three the most tenable options [3]. SR reaction offers higher energy efficiency since provides the maximum theoretical yield of hydrogen [9] although is a strongly endothermic process that requires an external supply of heat. POX reaction shows a fast start-up and quick response time, as well as a simple and compact design, which is desirable for automotive and mobile fuel cell applications [10]. However, the likelihood of hot-spot formation makes it difficult to control the reaction. Although being exothermic is an innate property of POX reactions, its major barriers can be expressed as relatively low hydrogen mole produced per mole of ethanol [3]. Oxidative steam reforming or autothermal reforming process is the combination of steam reforming and partial oxidation reactions. The addition of oxygen to steam reforming conditions allows achieving an equilibrium between hydrogen selectivity and energy efficiency, besides promoting the removal of inactive carbon species from the catalyst surface [11]. Therefore, proposing a solution to prevail the challenges of SR, POX, and ATR of ethanol comes into consideration. Such a solution requires to meet both objectives of increasing catalytic rate of favorable product (hydrogen) and minimizing coke formation.

Diverse catalytic systems have been investigated for catalytic steam reforming, including transition metals (Co, Cu, Ni) [12–14], noble metals (Pd, Au, Ru, Pt, Rh) [12,15], and bimetallic and ternary metallic combination of transition and noble metals [16,17]. Similar, several catalytic systems, such as packed or fluidized bed reactors or fluidized bed membrane reactors [18,19], with the focus on noble metals or transition metals were proposed for ATR [20–22]. However, both SR

and ATR of ethanol suffer from several limitations and challenges such as: i) catalyst deactivation [23], ii) formation of undesirable by-products (e.g. CH_4) [24], and iii) continuous heat supply especially for SR reactions [3].

On the other hand, and although POX reaction has not been so widely studied in different catalytic systems, the role of noble metals (Pt, Rh, Pd, Ru) [10,25] as well as non-noble metals (Ni , Co) [10,26] has been explored for their use as monometallic and bimetallic catalysts [27,28]. Moreover, the application of catalytic promoters could further enhance ethanol conversion to hydrogen. In the case of POX reaction, it was found that the addition of a V_2O_5 phase to a Pt catalyst improved its performance due to the V_2O_5 redox properties [29]. It was demonstrated that nitrogen promoted the catalytic activity of partial oxidation processes over vanadium oxide catalyst supported on nitrogen-doped TiO_2 [30]. Chimentao et al. [31] also explored the function of alkali promoter, Na, in a vanadium oxide catalyst. Sodium addition affected dispersion, reducibility and acidity of the catalyst and, although a high amount of sodium worked against catalytic activity, an increase in sodium loading decreased carbon deposition during reaction, extending catalyst lifetime.

The phenomenon of electrochemical promotion of catalysis (EPOC), also referred as non-faradic electrochemical modification of catalytic activity (NEMCA) [32,33], is described as an activation of a catalyst via back-spillover mechanism in which the promoter ions are supplied from an electro-active support (solid electrolyte) by introduction of a potential difference between support and surface of catalyst or electro polarization. Accordingly, the in-situ supply/removal of promoters can be continuously and reversibly controlled, under reaction condition. According to the recent literature, EPOC can contribute in solving various challenges faced in heterogeneous catalysis domain such as to alter the oxidation state of a catalyst, reversibly [34–36], to utilize carbon deposition for regeneration of a catalyst throughout the catalytic reaction [37], and to hinder the poisoning effect [38].

Application of EPOC resulted in electrochemical activation of various catalytic systems with the purpose of the hydrogen production. The processes of concern were methanol steam reforming [38,39], water-gas shift (WGS) [40,41] , and methane steam reforming [42,43] reactions. SR of methanol can be the most relevant case to ethanol reforming as both feedstocks categorized as primary alcohols, and the studied catalytic systems were Ni and Cu both supported on $K\beta Al_2O_3$ [38,39]. Most of these studies have shown the interest of EPOC in the H_2 production technology

1 as reviewed in recent publications [44,45]. Nonetheless, the commercial implantation of the EPOC

2 phenomenon has not been developed yet, being the poorly dispersed materials on the electrode,

3 the reactor configuration or the study of the adequate processes the main drawbacks [45].

4 A recent study has also recently shown the potential application of EPOC for SR of ethanol over

5 Pt-KβAl$_2$O$_3$ electrochemical catalyst. The reported increase in activity and selectivity of a Pt

6 catalyst in H$_2$ production was due to the electrochemical supply of the potassium ions from K-

7 βAl$_2$O$_3$. This resulted in significant increase in H$_2$ production rate, and removal of intermediate

8 carbonaceous species from the surface of catalyst via application of +2 V [46]. In addition, the

9 complete oxidation of ethanol reaction was studied using EPOC as a tool to enhance the

10 dehydrogenation of ethanol and the subsequent formation of acetaldehyde over Pt [47]. Tsiakaras

11 et al.[48] also conducted a study on a similar catalytic system and optimized the reaction conditions

12 for the maximum production of acetaldehyde. To date, no research on EPOC of the partial

13 oxidation of ethanol has been reported.

14 The present study aims to investigate for the first time in literature the application of EPOC

15 phenomenon to the partial oxidation of ethanol. In addition, steam reforming of ethanol was carried

16 out to compare to what extent the results of POX and SR of ethanol are varied with respect to

17 activity in hydrogen production. The optimal oxygen-to-ethanol and steam-to-ethanol, three

18 atmospheres of POX, SR, and ATR were investigated to assess the influence of the EPOC

19 phenomenon on the catalytic activity and catalytic stability. Furthermore, the reproducibility of

20 the EPOC phenomenon was investigated under ATR conditions under five short polarization

21 cycles and under a long-time polarization experiment to check the stability of the system in view

22 of possible practical application.

23 ## 2. Experimental section

24 ### 2.1. Electrochemical catalyst preparation

25 The electrochemical catalyst used consisted of a continuous, thin Pt film supported on an alkaline

26 solid electrolyte (K-βAl$_2$O$_3$, K$^+$ conductor), as the one used in a previous study [46]. Au, which

27 was chosen as a counter and pseudo-reference electrode due to its inertness, was first deposited on

28 one side of a 20-mm-diammeter, 1-mm-thick K-βAl$_2$O$_3$ (Ionotec) disc by applying a thin coat of

29 gold paste (Gwen Electronic Materials) following by calcination at 800 ºC for 2 h (heating ramp

4

1   of 5 ℃·min^{-1}). The working Pt electrode was deposited on the opposite side of the solid-electrolyte.

2   Pt thin film was deposited by impregnation of a H_2PtCl_6 water/2-propanol solution, as described

3   in detail elsewhere [49]. Finally, the electrode was again calcinated at 550 ℃ for 2 h (heating ramp

4   of 5 ℃·min^{-1}). The impregnated geometric area of the electrode was 2.01 cm^2 and its final Pt

5   loading was 1 mg·cm^{-2}. Prior to any catalytic activity measurement, a temperature programmed

6   reduction treatment was performed. Electrocatalyst was exposed to a 5% H_2 stream (Ar balance,

7   total flow = 100 mL·min^{-1} Standard Ambient Temperature and Pressure, SATP) from room

8   temperature to 550 ℃ (heating ramp of 5 ℃·min^{-1}).

9

10   **2.2. Catalytic activity measurements**

11   All catalytic activity measurements were carried out in an experimental setup used in previous

12   studies [49] with a well-known single chamber solid-electrolyte cell reactor configuration [50].

13   Two thermostated saturators, which contained ethanol (Panreac, 99.8% purity) and milli-Q water

14   respectively, were sparged with an Ar gas flow to feed the reactor. The Ar flow was controlled by

15   a set of mass flowmeters (Bronkhorst EL-FLOW) that in turn controlled the rest of the gases used.

16   These reaction gases (Praxair, Inc) were certificated standards (99.999% purity) of Ar (carrier gas),

17   H_2 (reducing agent), and O_2 (reactant gas). A double channel gas chromatograph (GC) (Bruker

18   450-GC) previously described [46] and connected on-line was used to analyse all reactant and

19   product gases. The detected products were hydrogen, carbon monoxide, carbon dioxide, methane,

20   ethylene and acetaldehyde.

21   Working, counter and reference electrodes were connected to an Autolab PGSTAT320-N

22   potentiostat-galvanostat (Metrohm Autolab) using gold wires (Alfa Aesar, 99.95% purity). In

23   order to perform the EPOC experiments, different electric potentials were applied between

24   working and counter electrodes and measured between working and reference electrodes (V_{WR}),

25   as it is generally proceeded in conventional three-electrode electrochemical cells [51,52].

26   All catalytic experiments were carried out at ambient pressure and at 550 ℃, with an overall flow

27   rate of 100 mL·min^{-1} (SATP). Partial oxidation, steam reforming and autothermal reforming of

28   ethanol reactions were studied by applying potentiostatic transients between +2 V and -1 V. In the

29   case of partial oxidation reactions, different inlet compositions (O_2:EtOH = 1:2, 1:3, 1:4) were

1   evaluated, keeping always a 3% ethanol composition. Ethanol steam reforming composition

2   consisted of 3% EtOH and 9% H_2O, Ar balance, whereas an inlet composition of 3% EtOH, 9%

3 H_2O, 1% O_2, Ar balance was used in autothermal reforming reactions.

4

3. Results and discussion

6

3.1. Electrochemical promotion of Pt catalyst for the partial oxidation of ethanol

8   The phenomenon of Electrochemical Promotion was first applied to the ethanol partial oxidation

9   reaction. For that purpose, potentiostatic transients experiments from +2 V to -1 V (for 115 min

10   each) were performed at 550 ºC. **Figure 1** shows the response of hydrogen production rate vs. time

11   during the application of various electrochemical potentials.

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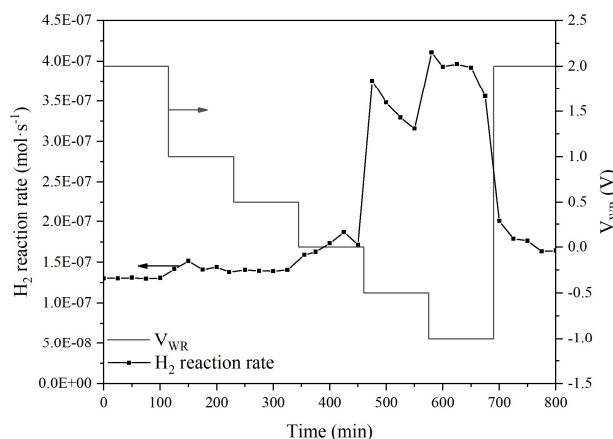
Figure 1. Potentiostatic transient response of hydrogen reaction rate as a function of applied potential
Inlet composition: 3% EtOH, 1% O_2, Ar balance. T = 550 ºC.

15   At the beginning and at the end of each experiment, a positive potential (V_{WR} = +2 V) was applied

16   to clean the catalyst surface and remove any present K^+ ions. This initial positive potential

17   application is required because some positive alkaline ions could spontaneously migrate to the

18   catalyst surface during the catalyst preparation and reduction steps. This was previously reported

19   for catalytic systems supported on alkaline ionic conductors, e.g., K-βAl_2O_3 [53]. After positive

20   polarization, the catalyst film is free of potassium ions, establishing in that way an unpromoted,

21   reference state.

6

1   **Figure 1** shows that a decrease in the applied potential below 0.5 V led to an increase in the

2   hydrogen production rate, i.e., the electrochemical supply of K^+ ions led to a strong activation of

3   the partial oxidation of ethanol on the Pt catalyst. This enhancement of the hydrogen production

4   rate through the presence of K^+ ions corresponded, according to the rules of electrochemical

5   promotion of catalysis, to an electrophilic behavior [33]. The electrophilic behavior is translated

6   into a hydrogen production rate increase due to a decrease in catalyst potential and catalyst work

7   function. In this case, the migration of positively charged potassium species weakened the Pt

8   chemical bond with electron-donor adsorbates (ethanol) and strengthened chemical bond with

9   electron-acceptor ones (oxygen). Similar behavior was reported in a previous study of methanol

10 partial oxidation using the same solid electrolyte, where methanol was identified as the donor

11 molecule and oxygen as the acceptor one [54].

12 On the other hand, it can be observed a relevant catalyst deactivation during the negative

13 polarization steps. Hence, after the initial catalyst activation, there was a decrease in the activity

14 probably due to the large formation of adsorbed intermediate reaction species. These intermediate

15 species that would further react and be decomposed are also capable of partially blocking some

16 the active sites. Catalyst deactivation has always been a major issue in partial oxidation reactions

17 and a certain amount of carbon deposit was measured on different catalysts surfaces [26,27].

18 Nonetheless, the decrease observed in **Figure 1** seems to be more likely due to an excess of acetate

19 or ethoxy species adsorbed on the catalyst surface [11,25], which would be further reacted into

20 acetaldehyde. In fact, an initial deactivation was observed at the beginning of the reaction in

21 previous catalytic studies [55–57], even if the catalysts performance remained stable after this

22 deactivation.

23 Finally, the application of +2 V at the end of the experiment resulted in removal of K^+ ions from

24 the catalyst surface back to the solid electrolyte, leading to a decrease in hydrogen production rate.

25 The reaction rate value returned to its initial state observed at the beginning of the experiments,

26 confirming a reversible EPOC effect. This effect was previously observed in an in-situ XPS study

27 on a Ni catalyst supported on K-βAl_2O_3 [58]. An intense K_{2p} signal was found under negative

28 potential of -2 V that disappeared almost immediately when potential was switched to a positive

29 value of +2 V. Similar hydrogen production rate values at the beginning and at the end of the

1   experiment not only showed the reversible nature of the promotional effect, but also a good

2   stability of the catalyst film through different polarization steps.

3   Following the procedure carried out in **Figure 1**, the ratio of oxygen-to-ethanol (O_2:EtOH) was

4   studied at different applied potentials (for 115 min each) at 550 ºC, as shown in **Figure 2**. Three

5   different O_2:EtOH ratios were evaluated, maintaining the composition of ethanol at 3%. In this

6   kind of transients, a steady-state catalytic rate value was obtained after few minutes of polarization.

7   In the cases that catalytic rate values were not stable, an average value was selected. In order to

8   evaluate the catalyst activation under EPOC, the reaction rate enhancement ratio, ρ, was calculated

9   using Eq. (1) [33]:

10

$$\rho = \frac{r}{r_0} \tag{1}$$

11   where r denotes the promoted ($V_{WR} < 2$) steady state catalytic rate value at each potential step, and

12   r_0 the unpromoted ($V_{WR} = 2$) catalytic rate. Under all the explored O_2:EtOH molar ratios, hydrogen

13   reaction rates values always showed an electrophilic EPOC behavior, asserting the positive

14   influence of the potassium ions and the catalyst work function decrease. Nonetheless, in the case

15   of 1:2 ratio, a maximum value was reached at -0.5 V. Further potential decrease to -1 V led to a

16   decrease in the catalytic activity. At this molar ratio, a high O_2 coverage could be restricting ethanol

17   adsorption on the catalyst surface. At negative potentials (-1 V), the presence of K^+ strengthened

18   the Pt chemical bond with oxygen while weakening with ethanol. For that reason, ethanol

19   molecules could be limited in the catalyst surface due to the large coverage of oxygen. On the

20   other hand, and as previously reported while working with alkali conductors [54], Pt impregnated

21   films could form and store potassium surface compounds, blocking part of the catalyst surface and

22   decreasing the number of Pt active sites. In these cases, the nature of the EPOC phenomenon relies

23   also on the electrocatalytic activity of the catalyst film and not only on the kinetics order of

24   acceptor and donor molecules. Working at a negative potential such as -1 V could lead to an excess

25   of promoter coverage on the catalyst surface that could poison Pt active sites [39].
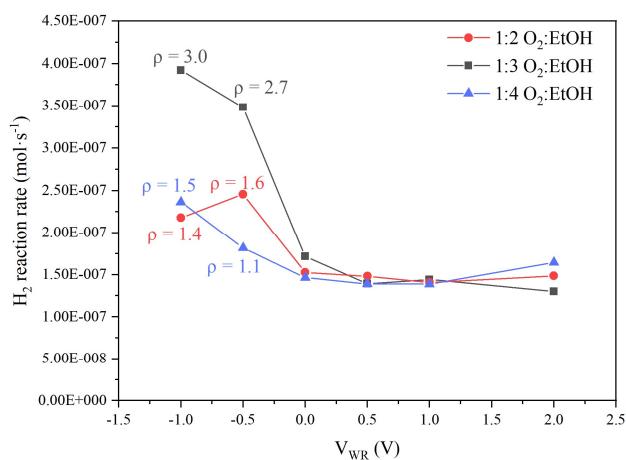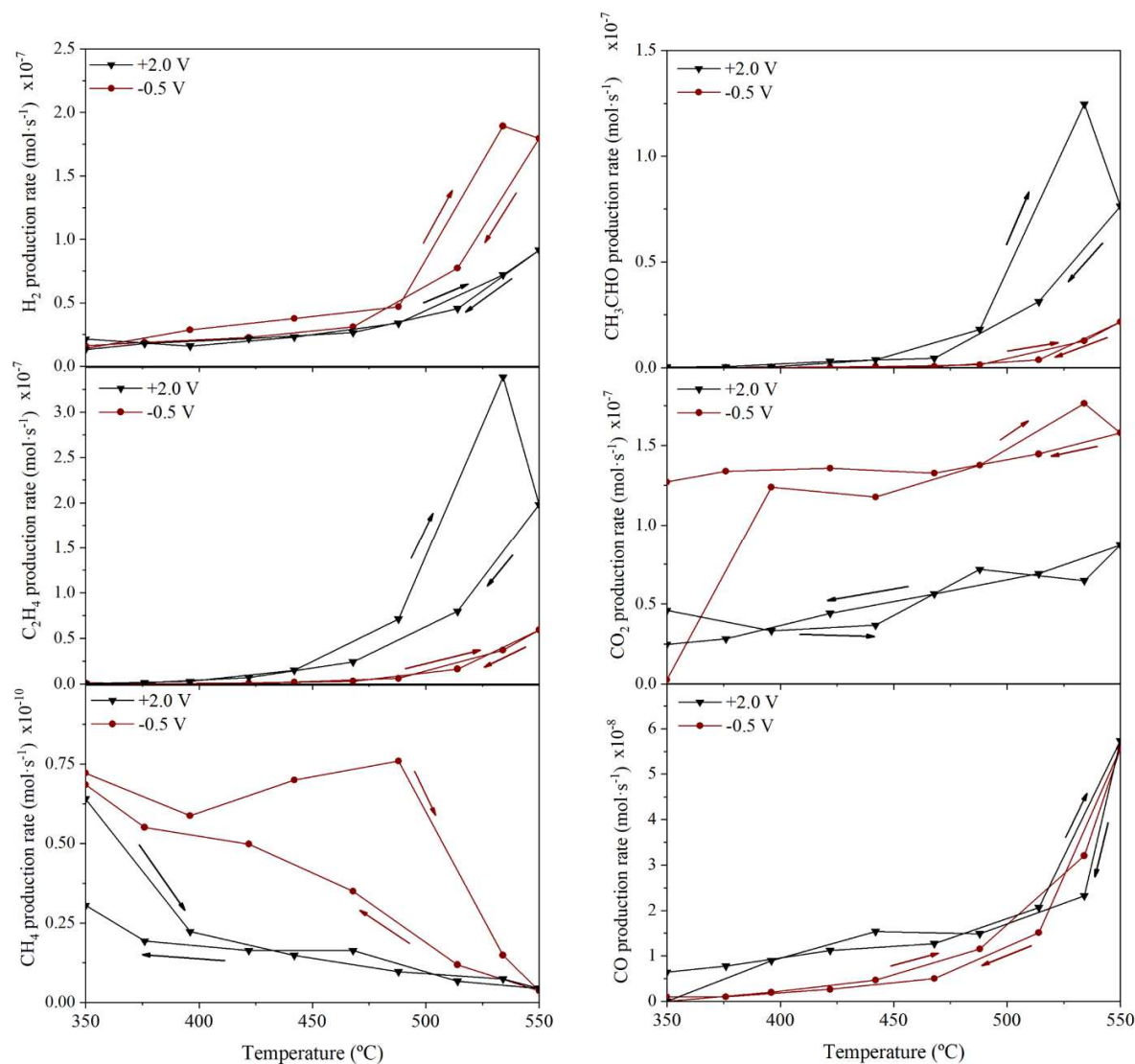
Figure 2. Hydrogen production rate and vs. applied potential at three different O_2: EtOH molar ratios. Inlet composition: 3% EtOH. T = 550 ºC.

According to catalytic partial oxidation of ethanol studies [59], the oxygen-to ethanol molar ratio affects directly on the hydrogen yield, which is dramatically reduced at high ratios since the competitive hydrogen oxidation reaction is enhanced along with the ethanol complete oxidation reaction. For that reason, O_2:EtOH molar ratios below 0.5 were selected in this work, finding the best electrocatalytic performance while feeding the reactor with 1:3 O_2:EtOH molar ratio. The migration of potassium ions favors the oxygen adsorption (electron-acceptor) rather than ethanol adsorption (electron-donor) into the catalyst surface. Thus, high molar ratios could result in a large coverage of oxygen that could limit the presence of ethanol in the catalyst surface while very low molar ratios could not provide enough oxygen. For that reason, 1:3 O_2:EtOH molar ratio presented the highest catalytic activity and EPOC increase and it was selected as the optimal reaction atmosphere for the rest of experiments. In the same way, an optimal polarization value of -0.5 V was selected for subsequent reaction experiments since a further negative potential application of -1 V may conditioned the long operation life of the electrochemical cell with no relevant increase in the catalytic reaction rate.

3.2. Insight of the promotional effect on the partial oxidation reaction mechanism

The variation of the different products rates: hydrogen, carbon monoxide, carbon dioxide, methane, ethylene and acetaldehyde at unpromoted (+2 V) and promoted (-0.5 V) conditions was investigated through temperature programmed experiments, as shown in **Figure 3**. In these experiments, products reaction rates were followed-up via gas chromatography while applying a
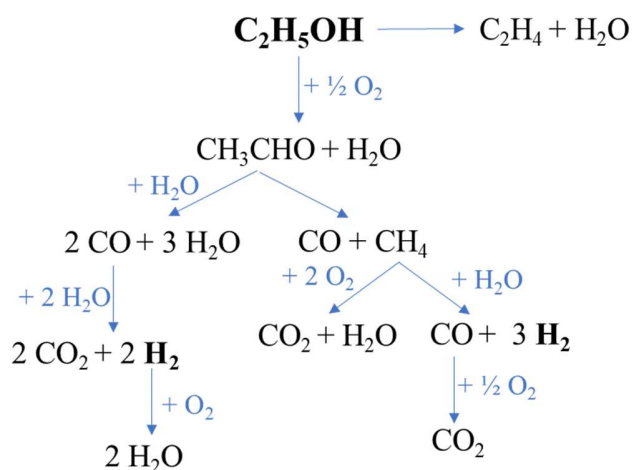
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1   constant potential (+2 V or – 0.5 V) and programming a 2 ºC·min⁻¹ ramp temperature from 350 ºC

2   to 550 ºC and then back to 350 ºC.

3

7

8   Due to the presence of a C-C bond in the ethanol molecule and the oxygen, the possible reaction

9   pathways that may occurred on the system are complex. In fact, Sawatmongkhon et al. [59]

10   proposed 21 reactions that might take place during partial oxidation of ethanol. According to

10

1   literature, the possible combinations due to the number of potential by-products and its further

2   transformations are quite numerous, and depend strongly on the support material, metal catalyst,

3   and on the reaction conditions [60], playing a dominant role in the scission of the C–C bond and

4   the final product distribution [61]. On the basis of previous studies [60,62,63] and the products

5   experimentally measured here, the possible reaction mechanism (schemed in **Figure 4**) could be

6   developed as follows. The oxidation dehydrogenation and dehydration of ethanol are the two initial

7   competitive steps on the reaction mechanism. Following the first route, ethanol is adsorbed on Pt

8   catalyst surface, where acetaldehyde is produced due to the presence of oxygen. Acetaldehyde is

9   then reformed and decomposed into methane and monoxide carbon, which would be further

10   oxidized and reformed into hydrogen.

$$C_2H_5OH \longrightarrow C_2H_4 + H_2O$$
$$\downarrow + \tfrac{1}{2}\,O_2$$
$$CH_3CHO + H_2O$$
$$+\,H_2O \swarrow \qquad \searrow$$
$$2\,CO + 3\,H_2O \qquad CO + CH_4$$
$$+\,2\,H_2O \downarrow \qquad +\,2\,O_2 \swarrow \qquad \searrow +\,H_2O$$
$$2\,CO_2 + 2\,\mathbf{H_2} \qquad CO_2 + H_2O \quad CO + 3\,\mathbf{H_2}$$
$$\downarrow +\,O_2 \qquad\qquad\qquad\qquad \downarrow +\tfrac{1}{2}\,O_2$$
$$2\,H_2O \qquad\qquad\qquad\qquad CO_2$$

11

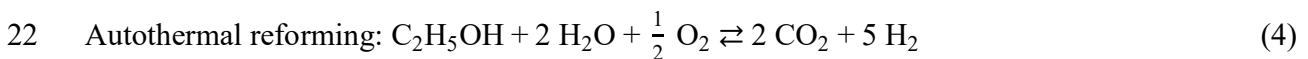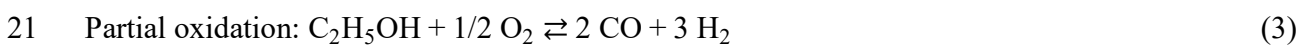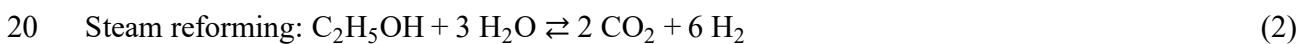12   **Figure 4.** Reaction mechanism scheme for partial oxidation of ethanol.

13

14   As observed in previous catalytic studies [56,64,65], at the explored temperature range, the

15   oxidation dehydrogenation and dehydration reactions can lead to noticeable amounts of

16   acetaldehyde, water or ethylene. In addition, the formation of carbon monoxide, which is

17   associated with hydrogen generation, is favored while increasing temperatures [59,64]. However,

18   it can be observed that the effect of the electrochemical promotion could allow its activation to

19   occur at lower temperatures increasing H_2 production. Hence, as shown in **Figure 3**, and under

20   unpromoted conditions (+2 V), it can be observed the pronounced increase in acetaldehyde and

21   ethylene production rates by temperature. The oxidation dehydrogenation and dehydration

22   reactions, which are the first steps of the reaction mechanism, are activated by temperature.

11

Nonetheless, this activation is not clearly observed in further reaction products such as hydrogen. Acetaldehyde reforming and decomposition reactions become the rate-limiting step, so the reaction mechanism is limited. However, the presence of K^+ ions on the catalyst surface (under promoted conditions, i.e., -0.5 V) led to a strong activation of the hydrogen production rate at lower temperatures. According to these results, one could suggest that polarization activated ethanol oxidation dehydrogenation route leading to an increase in the H_2 production rate instead of ethylene formation. Hence, the presence of potassium ions enhances the initial acetaldehyde formation and further reforming and decomposition reactions, and hence the rest of the mechanism, giving as a result the increase in hydrogen production rate. Since ethanol dehydration reaction route does not produce hydrogen, it was demonstrated the beneficial effect of EPOC application on partial ethanol oxidation, that favors ethanol oxidation dehydrogenation route that leads to hydrogen production instead of ethanol dehydration one.

3.3. Effect of the steam addition: evaluation of steam reforming, partial oxidation and autothermal reforming reaction conditions.

The effect of the addition of steam to the system was evaluated. For that purpose, three different reaction conditions: steam reforming, partial oxidation and autothermal reforming (Eq. (2-4)) were studied.

The production rates vs. time were followed-up under unpromoted (+2 V) and promoted conditions (-0.5 V), modifying the reaction conditions every 140 min, as shown in **Figure 5**.

Steam reforming: $C_2H_5OH + 3\ H_2O \rightleftarrows 2\ CO_2 + 6\ H_2$ (2)

Partial oxidation: $C_2H_5OH + 1/2\ O_2 \rightleftarrows 2\ CO + 3\ H_2$ (3)

Autothermal reforming: $C_2H_5OH + 2\ H_2O + \frac{1}{2}\ O_2 \rightleftarrows 2\ CO_2 + 5\ H_2$ (4)

For all three reaction conditions, the promotional effect presented an electrophilic behavior since the presence of K^+ ions activated all reaction mechanism towards hydrogen production, favoring the complete conversion of intermediate products such as acetaldehyde, ethylene or methane that were not observed under promoted conditions.
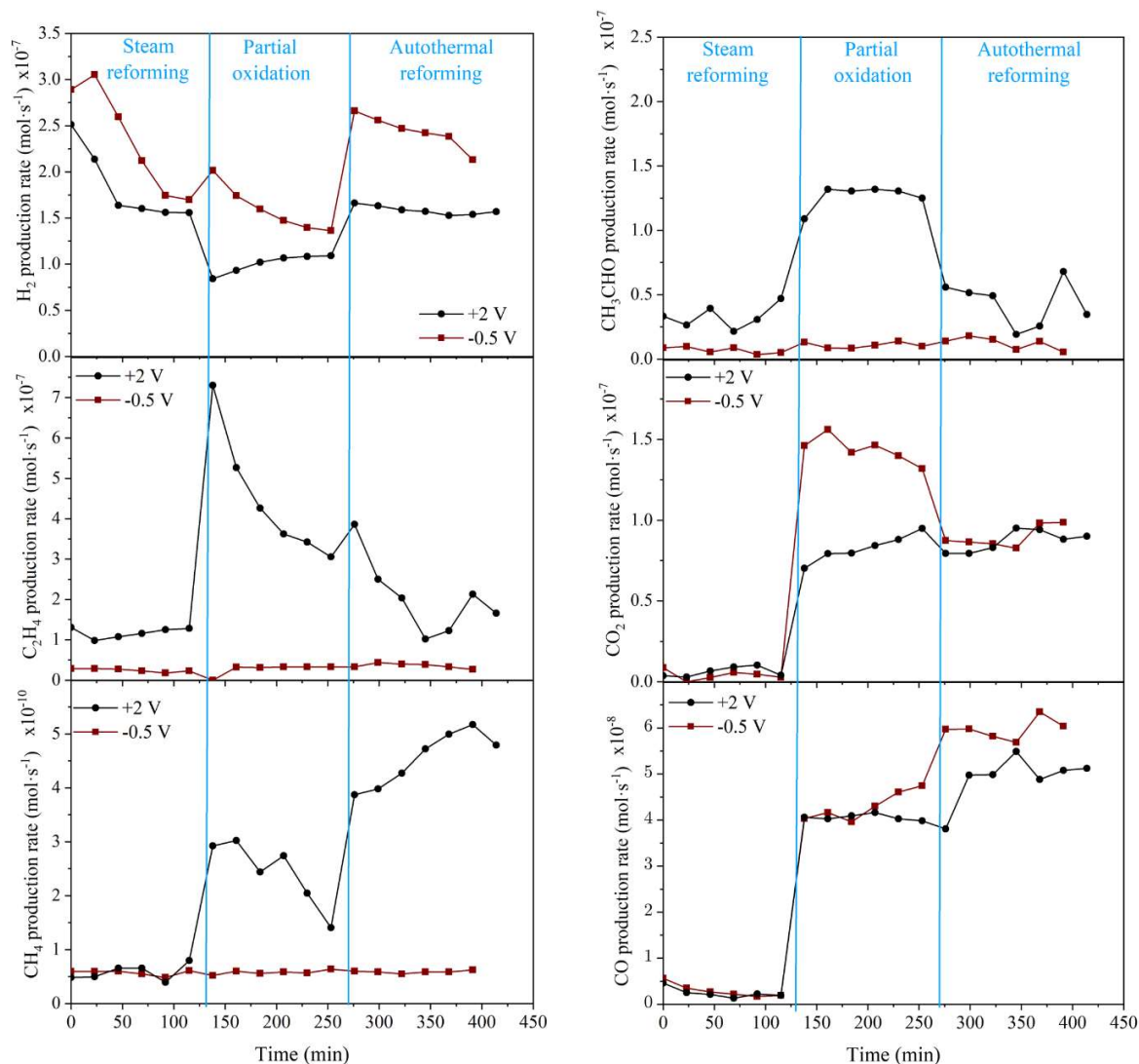
Figure 5. Products reaction rates vs. time. Changes in the atmosphere. Steam reforming: 3% EtOH, 9% H_2O, Ar balance. Partial oxidation: 3% EtOH, 1% O_2, Ar balance. Autothermal reforming: 3% EtOH, 9% H_2O, 1% O_2, Ar balance. T = 550 ºC.

As expected, under unpromoted and promoted conditions, steam reforming presented a higher catalytic activity towards hydrogen production, since it provides the maximum theorical yield of hydrogen [9]. However, hydrogen production rate decreased in a more pronounced way under this atmosphere. In a previous study, where ethanol steam reforming reaction was studied using the same electrocatalyst configuration [46], it was observed a catalytic activity decrease along the

13

time, especially pronounced under promoted conditions. This decrease was attributed to the continuous formation and adsorption of intermediate carbonaceous species that block Pt active sites. Intermediate carbonaceous species are induced by the presence of potassium ions on the catalyst surface, being the reason of the fast decrease under promoted species.

Under partial oxidation conditions, and as already discussed, ethanol oxidation dehydrogenation and ethanol dehydration reactions are activated at this temperature (T = 550 ºC), leading to large acetaldehyde and ethylene production rates under unpromoted conditions, while hydrogen production rates are limited since acetaldehyde reforming and decomposition reactions act as the rate-limiting step. Under promoted conditions, hydrogen production rates increased since the presence of K^+ ions activated the acetaldehyde reforming route as previously discussed. As already observed in previous studies [26], and under unpromoted conditions, higher acetaldehyde production rates were achieved by replacing steam with oxygen, although its further decomposition was hindered leading to a decrease in hydrogen selectivity. Nonetheless, even if acetaldehyde decomposition was enhanced via polarization, partial oxidation provides a lower theoretical yield of hydrogen. Although partial oxidation showed a more stable behavior, the obtained catalytic activity is lower than the two other reactions.

Similar justification can be presented for CO formation rate in partial oxidation and autothermal reforming with negative potential. Compared to CO production rate, a noticeable increase can be observed under partial oxidation and autothermal reforming, though the maximum CO formation rate is approximately 2.6 and 3.6 times lower than the correlated point for hydrogen production rate under negative potential for POX and ATR. Acetaldehyde, ethylene, and methane production rate exhibited a quasi-steady state behavior in all three reaction conditions with relatively low magnitude under promoted condition. Such a behavior can prove that the catalytic activity at promoted state is independent from the exposed reaction conditions, and a small fraction of the product distribution can be associated with the abovementioned species.

The combination of steam reforming and partial oxidation resulted in autothermal reforming with a pronounced increase in hydrogen formation rate; moreover, the experimentally observed catalytic deactivation is less important vs. the steam reforming conditions, due to the presence of some O_2 in the gas atmospheres which favors the oxidation of intermediate and carbonaceous reactions species. Analysis of the rate enhancement ratio (ρ) for H_2 production reveals that the

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1 highest value is attained under autothermal reforming conditions achieving a value of 1.6 under

2 steady state conditions (autothermal reforming, $\rho = 1.6$; steam reforming, $\rho = 1.1$; partial oxidation,

3 $\rho = 1.3$). Taking into account these results, the autothermal reforming conditions were selected as

4 the optimal ones (activity, stability and magnitude of EPOC enhancement) for subsequent stability

5 and reproducible reaction experiments, as shown below.

6

7 **3.4. Reproducibility and stability tests for autothermal reforming conditions**

8 The stability and reproducibility tests were conducted by two different kind of reaction

9 experiments: short- and long-time polarization experiments. During short-time polarization, H_2

10 production rate was monitored through 30 min cycles in a sequence of unpromoted (+2 V)

11 followed by promoted (- 0.5 V) state for an overall exposure time of 150 min (**Figure 6a**). Long-

12 time polarization lasts for 1100 min with initial unpromoted step (+2V) for 150 min, subsequent

13 promoted state (- 0.5 V) for 720 minutes (12 h), following the second unpromoted state step for

14 120 min, and finally with the last promoted step for 110 min (**Figure 6b**).

a)

b)
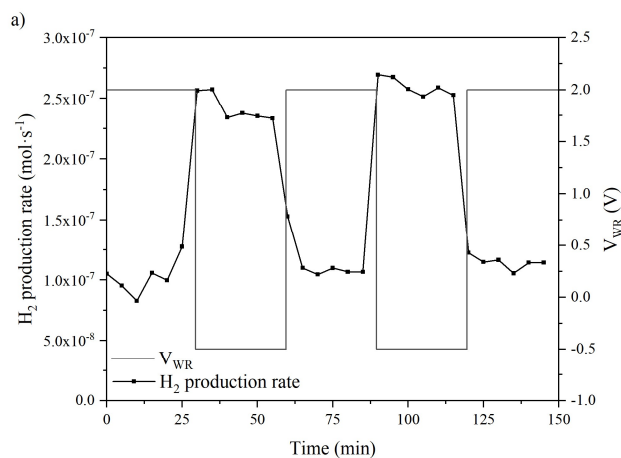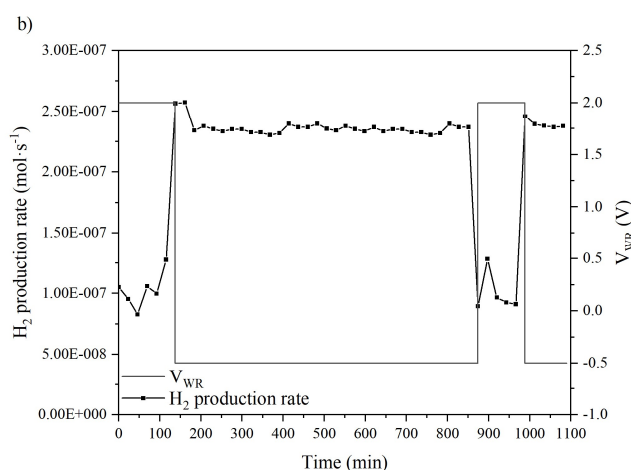
Figure 6. Autothermal reforming stability tests: hydrogen reaction rate vs. time. a) Short-time (30 min each) polarization cycles. b) Long-time negative polarization. Inlet composition: 3% EtOH, 9% H_2O, 1% O_2, Ar balance. T = 550 ºC.

The results of short-time polarization reveal that the attained EPOC effect is electrophilic, reversible, and reproducible which agrees well with the findings of **Figure 5**. As it has been remarked in all previous experiments and all different reaction conditions, the electrochemical supply of potassium enhanced hydrogen production rate. Hence, as already observed, potassium ions migration during the first seconds of polarization induced hydrogen production rate activation response while switching from unpromoted to promoted states. Moreover, hydrogen production rates were reproducible, leading to the same values while the same polarizations were applied. On the other hand, long term negative polarization also showed similar behavior as the short-time one with respect to EPOC effect. Contrary to the steam reforming conditions, the system shows a quasi

16

steady state H$_2$ production rate during the negative polarization, proving that the catalytic deactivation is negligible and that there is no loss of potassium under the explored EPOC conditions. As it has been already reported [26,66], the continuous formation and adsorption of intermediate carbonaceous species could block catalyst active sites under steam reforming conditions leading to significant activity losses (resulting in a 50% drop of ethanol conversion in some cases [62,67]). Nonetheless and, in all cases, the addition of oxygen (autothermal reforming atmosphere) produced an appreciable improvement in the catalyst stability, as it has been proved comparing our previous study with those results shown in **Figure 6**, which in addition is compatible with the EPOC enhancement effect.

4. Conclusions

To recapitulate, this study demonstrated the contribution of EPOC effect on remarkable enhancement of hydrogen production rate under ethanol partial oxidation conditions. Hence, the electrochemical supply of potassium ions into Pt catalyst film increases the hydrogen production rate due to a decrease in catalyst potential and catalyst work function. The migration of potassium ions weakened the Pt chemical bond with electron-donor adsorbates (ethanol) and strengthened chemical bond with electron-acceptor ones (oxygen).

As observed from temperature programmed reaction experiments, the negative polarization activated ethanol oxidation dehydrogenation into acetaldehyde and its further acetaldehyde reforming and decomposition reactions, and hence the rest of the mechanism for hydrogen production, allowing the further oxidation of acetaldehyde that could not be completed without the presence of potassium promoter ions. The promotional effect favored this route instead of ethanol dehydration reaction, which led to ethylene formation. It demonstrates the interest of EPOC for in-situ tuning catalyst selectivity toward a certain desired product along with having a better mechanistic view on involved catalytic reactions.

The expanding of this study to steam reforming and autothermal reforming conditions demonstrates that this latter reaction atmosphere shows the best behavior in terms of catalytic activity, stability and EPOC enhanced effect achieving an increase in the H$_2$ production rate of 1.6 times vs. the un-promoted catalyst state. The reproducibility of the EPOC phenomenon was fully demonstrated as well as the stability of the catalyst film and promotional phases under electro-

17

promotion conditions. These results show potential for the practical use of the electrocatalytic configuration in the H_2 technology as well as the operando controlling of the H_2 production rate for mobile processes.

Credit authorship contribution statement

Arash Fellah Jahromi: Conceptualization, Methodology, Investigation, Writing original draft, Writing-review & editing, Visualization, Data curation. **Estela Ruiz-López:** Conceptualization, Methodology, Investigation, Writing original draft, Writing-review & editing, Visualization, Data curation. **Fernando Dorado:** Supervision, Writing-review & editing, Funding acquisition, Data curation. **Elena A. Baranova:** Supervision, Writing-review & editing, Funding acquisition, Data curation. **Antonio de Lucas-Consuegra:** Supervision, Writing-review & editing, Funding acquisition, Data curation.

Declaration of Competing Interest

There are no known competing financial interests to declare.

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