

New Trends of Alkali Promotion in Heterogeneous Catalysis: Electrochemical Promotion with Alkaline Ionic Conductors

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Abstract Chemical promotion obtained with the addition of alkalis to a metal supported catalyst induces effects on the catalytic activity very similar to those of electrochemically supplied alkali ions through the concept of electrochemical promotion of catalysis. Despite of the functional identity and the origin between two ways of promotion analyzed here (chemical and electrochemical), which follow the same general rules, the usefulness of the latter is clear. In this review the most important and recent contributions of Electrochemical Promotion with alkaline ionic conductors (Na^+ and K^+ conductors) in heterogeneous catalysis have been analyzed. The possibility of in situ controlling the alkali promoter coverage on the catalyst under working conditions lead to new opportunities from both: fundamental and more applied point of view. The optimization of catalytic activity and selectivity, the activation of a catalyst at lower reaction temperatures, the permanent electro-promotional effect or the regeneration of a catalyst at fixed reaction conditions are some of the novel contributions discussed here. Due to the wide use of alkali ions as electronic promoters in heterogeneous catalysis the aim of this review is to bring closer this fascinating and novel phenomenon to the catalysis scientific community.

Keywords Electronic promoters · Alkali promotion · Electrochemical promotion · Ionic conductors · Active catalyst supports · EPOC · Back-spillover

1 Introduction

Promoters play a key role in heterogeneous catalysis and their use is of paramount importance in the design of successful commercial catalysts for industrial applications [1]. Two kinds of promoters can be used in heterogeneous catalysis: structural promoters and electronic promoters. The former enhance and stabilize the dispersion of the active phase on the catalyst support. The latter enhance the catalytic properties of the catalytic phase itself. This review is focused on the second kind of promoters, which are typically alkali ions that can be added chemically or electrochemically to a catalyst [2]. The effect of these promoters is based on their ability to modify chemisorption properties of the catalyst and hence to significantly alter the chemisorptive bond strength of reactants and intermediates. These effects may be originated from either electronic interactions, i.e., the modification of electron density of alkali-promoted metal surfaces, and/or from electrostatic interactions associated with alkali-metal ions, and/or from site blockage [3]. There is a very rich literature and comprehensive book [4] on the role of promoters in heterogeneous catalysis. In the majority of cases, it has been found that alkali addition results in a significant improvement of catalytic performance and that the promotional effect, which often depends on the size of the dopant atom, is maximized for a certain alkali content on the catalytic surface [5, 6]. Classical examples of industrially important catalytic reactions promoted by alkalis are the Fischer–Tropsch synthesis of hydrocarbons and the ammonia synthesis from N_2 and H_2 [7]. Commercial catalysts for ethylene epoxidation are also typically promoted by alkali-metal salts that are incorporated during the catalyst preparation step [8]. One can also find in literature a great number of research studies of alkali promotion for a wide

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range of catalytic systems. For instance, recent reports have shown substantial improvements in the water gas shift reaction when doping alkali (Na, Li, K) to Pt/CeO₂ [9, 10], Pt/TiO₂ [11–13], Pt/ZrO₂ [14, 15], Pt/Al₂O₃ [16] and Pt supported on carbon nanotubes [17]. The selective catalytic reduction of NO_x (SCR) has also widely studied in literature by Pt-alkali promoted systems. Hence, it has been shown that NO reduction rate increases by up to two orders of magnitude accompanied by large increases of N₂-selectivity over optimally promoted Pt catalysts by Li, Na, K, Rb, Cs or Ba, [18–21]. The promotional effect of alkali ions has also been demonstrated in other metal catalysts such as Pd [22], Rh [23, 24], Ru [25], Cu [26], Au [27], on a wide variety of catalytic reactions. These are only several examples of the very rich literature related to alkali promotion in heterogeneous catalyst. However, in all these previous examples a fixed amount of alkali promoter is chemically added during the preparation step of the catalyst. In the last years the phenomenon of electrochemical promotion of catalysis (EPOC) has shown to be an useful tool for the electrochemical addition of promoter ions to a catalyst surface [2]. In this case the addition of the promoter to the catalyst can be done in situ, during the catalytic reaction itself. Hence, the amount of alkali promoter can be easily modified (and thus controlled) by the external imposition of an applied electrical potential or current, which allows the electrochemical pumping of promoter ions from the catalyst support (solid electrolyte). This innovative concept that has been developed by Vayenas and co-workers [2] occurs when a catalytic reaction takes place on a catalyst film which is in contact with a solid electrolyte support. These kinds of materials have the ability to selectively transport ions in a wide temperature range between 25 and 1,000 °C. If the solid electrolyte is a cationic conductor material such as (NASICON, Na-βAl₂O₃ or K-βAl₂O₃), the application of a cathodic polarization between the catalyst film (which also behaves as a working electrode) and a second electrode (counter electrode) deposited on the other side of the solid electrolyte allows the electrochemical migration of the alkali ions (Na⁺ or K⁺) to the catalyst surface (phenomenon denoted as back-spillover). This concept represented on the Fig. 1, allows the electrochemical addition of electronic promoters, anionic ions (O²⁻) or cationic ions as in Fig. 1 (K⁺), to a catalyst surface during working conditions, instead of its chemical addition during the preparation step of the catalyst. One can find in literature very interesting reviews from more fundamental to more applied aspects related to the EPOC phenomenon [2, 28–35]. However, these previous reviews have been mainly focus on the use of anionic ions (O²⁻) conductors materials such as yttria-stabilized zirconia (YSZ) as a solid electrolyte. Due to the wide use of alkali ions as electronic promoters in heterogeneous

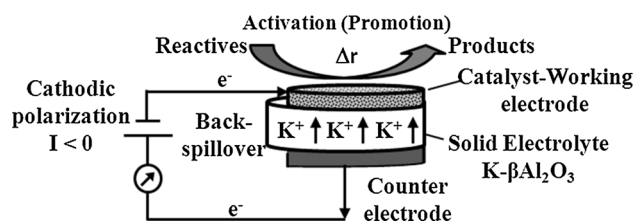
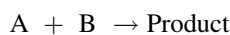


Fig. 1 The scheme of the electrochemical cell for electrochemical promotion studies with an alkali ionic conductor (K⁺ conductor) solid electrolyte

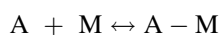
catalysis the aim of this review is to bring closer the EPOC phenomenon to the catalysis scientific community by the analysis of the most important and recent contributions of electrochemical promotion of catalytic reactions with alkaline conductors (Na⁺ and K⁺ conductors). Hence, this manuscript summarizes the most relevant aspects to understand the alkali electro-promotional effect of catalysts from its origin and mechanism to finally present high impact recent contributions of the alkali-EPOC phenomenon to the catalysis field.

2 The Effect of Chemical and Electrochemical Addition of Alkalis on the Chemisorption Properties of Catalysts

Catalysis and promotion are intimately related to the phenomenon of chemisorption. For a catalytic reaction to take place on a catalyst surface:



it is necessary that at least one of the reactants, and usually both, can chemisorb on the catalyst surface:



where M is a site on the catalyst surface. Langmuir was the first to model chemisorption phenomenon and to relate the surface coverage of the adsorbate with the catalytic activity leading to the well known Langmuir–Hinshelwood–Hougen–Watson (LHHW) kinetics for catalytic process [36]. The addition of promoters can affect the electronic state of the catalyst leading to significant changes in the work function, ϕ , of the catalyst surface and hence on its chemisorption properties. The work function ϕ (eV/atom), is one of the fundamental electronic properties of a metal surface and it can be defined such as the minimum energy required to extract one electron from the surface, when the surface is electrically neutral; i.e. the energy to bring an electron from the metal Fermi level to a distance of a few micrometers outside the metal surface so that image force interactions are negligible. Particularly in the case of alkali

ions (Na^+ , K^+), electropositive promoters, its addition to a metal particle cause a decrease in the work function of surfaces while electronegative promoters (e.g. O^{2-} ions) increase it. An example of this is the effect of alkali addition on Ru (0001) and Ru (1010) single crystals [37]. For low alkali metal coverage an initial decrease of the work function (by almost 4 eV) is observed. Thus, upon adding electronic promoters (e.g. alkali ions) on the catalyst surface, the chemisorptive bond strength of reactants and intermediates is modified and the catalytic kinetics are usually changed dramatically.

For the case of electrochemical addition of promoters to an heterogeneous catalyst, through the concept of EPOC, the effect on catalyst chemisorption and on reaction kinetics is exactly the same as the chemical addition of electronic promoters [2, 29]. Hence, it has been reported that the EPOC phenomena can be used to control the work function (ϕ) of gas-exposed metal surfaces. In 1990 Vayenas et al. [38] used the Kelvin probe technique to in situ measure the controlled variation of catalyst work function under EPOC conditions and to investigate the metal-solid electrolyte interface. They showed that work function changes on a catalyst supported on a solid electrolyte (as represented on Fig. 1) upon changing the ohmic-drop free change in the working electrode potential (U_{WR}) can be calculated by the Eq. (1):

$$\Delta\phi = e\Delta U_{\text{WR}} \quad (1)$$

In the last two decades, the Eq. (1) has been confirmed both theoretically and experimentally by several techniques [2]. It has been concluded that changes in the work function are due to the electrochemically induced and controlled migration of ions from the solid electrolyte onto the gas-exposed catalyst electrode surface. These back-spillover species form an effective double layer, which can thus dramatically influence catalytic reactions taking place at that gas-exposed interface, leading to the effect of electrochemical promotion.

Then, as commented above, upon varying the work function (by chemical or electrochemical addition of an electronic promoter) chemisorption properties of metal surface are changed. At the molecular level, this is a consequence of direct electrostatic interactions between adsorbed molecules and the electric field created by the coadsorbed promoter and indirect interactions due to the modification of the binding state of adsorbed reactants near the Fermi level of the metal. Hence, two rules derived by considering lateral attractive and repulsive interactions of co-adsorbed reactants and promoters were established [39, 40]:

-Increasing work function (by addition of electronegative promoters) strengthens the chemisorptive bond of electron donor adsorbates (D) and weakens the chemisorptive bond of electron acceptor adsorbates (A).

-Decreasing work function (by addition of electropositive promoters) weakens the chemisorptive bond of electron donor adsorbates (D) and strengthens the chemisorptive bond of electron acceptor adsorbates (A).

Alkali ions are electropositive promoters and, therefore, may act by enhancing chemisorption of electron acceptor species (decreasing work function), for example carbon monoxide and oxygen, and/or by suppressing chemisorption of electron donors, such as olefins and hydrogen [2]. A recent study related to the effect of electrochemical addition of alkali ions on the chemisorption properties of Pt catalyst can be found on reference [41]. In this work the chemisorption properties of a Pt catalyst deposited on $\text{K}-\beta\text{Al}_2\text{O}_3$ solid electrolyte (source of electro-positive potassium ions) were investigated at varying catalyst potential (V_{WR}) i.e., at varying potassium coverage on the Pt surface, via the isothermal titration technique (Fig. 2). In this experiment carried out at 250 °C, the Pt catalyst was firstly exposed to O_2 for 15 min (at fixed potential). Then, the reactor was purged with pure He for 4 min to remove gaseous O_2 . Subsequently, the reactor was fed up with C_3H_6 , and the amount of oxygen remaining (adsorbed) on the Pt surface (N) was obtained by integrating the area of the CO_2 peak in the reactor effluent. The variation of the CO_2 formation vs. time during the purge with C_3H_6 for each catalyst potential is shown on the Fig. 2. By integrating the area of the CO_2 peak, one can measure the oxygen remaining on the surface (N) versus the applied catalyst potential (inset Fig. 2). It can be clearly observed at the same time that the catalyst potential decreased, the CO_2 formation during the purge with C_3H_6 as well as the width of the CO_2 peak strongly increased. Thus, as the catalyst potential decreased and hence the potassium coverage on the Pt catalyst increased, there was an enhancement of the strength of the Pt–O bond during the isothermal titration experiment. It leads to both an increase of the amount of oxygen remaining on the surface (N) after the desorption step, and a time prolongation in the CO_2 formation during the purge with propene. Then is clear that the presence of potassium ions on the Pt catalyst surface strongly modified chemisorption properties of the Pt catalyst, e.g., O_2 chemisorbed molecules increased by approximately a factor 20 on the Pt electro-promoted surface (by K^+ ions). One can find in literature many other studies related to the effect of electrochemical addition of alkali ions on chemisorption properties of a catalyst. For instance Williams et al. [42] studied the electro-promotional effect of Cu catalyst deposited on $\text{Na}-\beta\text{Al}_2\text{O}_3$ on the catalytic reduction of NO by CO. The spectroscopy data clearly showed that the origin of the observed promotional effect by electrochemical pumping of Na^+ to the Cu catalyst (increasing the NO reduction activity and N_2 selectivity) was due to the strengthening of the metal-N bond

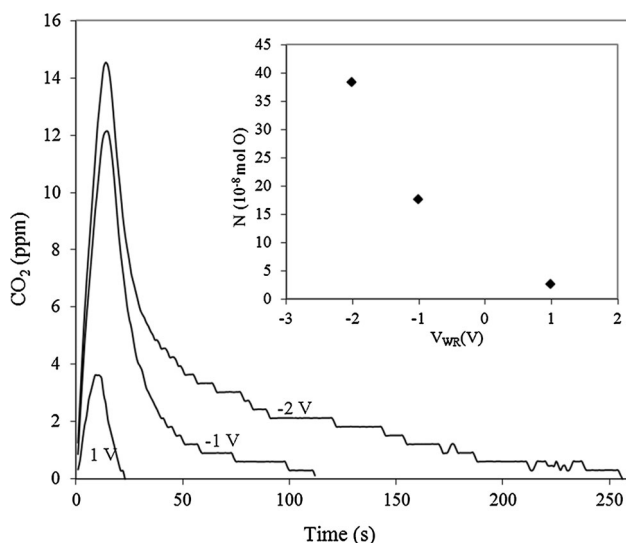


Fig. 2 The effect of the catalyst potential on CO_2 formation during the isothermal surface titration of oxygen by C_3H_6 at 250°C on Pt- $\text{K}\beta\text{Al}_2\text{O}_3$. *Inset* influence of the catalyst potential on the mass of reactive oxygen adsorbed on the Pt surface. Reprinted with permission from Ref. [41]. Copyright 2014 Elsevier

(increasing the NO coverage) and the weakening of the N–O bond (facilitating the NO dissociation). Guided by these results Konsolakis et al. [19] synthesized conventional dispersed Pt/ Al_2O_3 catalysts that when optimally promoted by Na, exhibited very large enhancements of both activity and selectivity showing the analogy between the two ways of promotion.

3 Electrochemical Promotion with Alkaline Ionic Conductors

3.1 Background

The phenomenon of electrochemical promotion with alkali ions has been widely studied in literature. A great number of catalysts and chemical reactions have been investigated with different kinds of alkaline ionic conductors materials (Na^+ , K^+ conductors), especially by using Na- $\beta\text{-Al}_2\text{O}_3$, K- $\beta\text{-Al}_2\text{O}_3$ and NASICON (Sodium Super Ionic Conductor) derived materials. One can find an excellent review on the use of these kind of ionic conductor materials as catalyst supports [35].

The Na- β -alumina family, a series of compounds in the $\text{Na}_2\text{O-Al}_2\text{O}_3$ system, is one of the most important groups of solid electrolytes that have been used in alkali electro-promotion studies. This material of excellent Na^+ ionic conductivity has been used in several reactions such as propane oxidation [43], CO oxidation [44], ethylene

Table 1 Some of the most relevant contributions in the history of EPOC with cationic conductors

Year	Description	Reference
1991	First report of EPOC using Na^+ conductor (Pt/ $\text{Na-}\beta\text{Al}_2\text{O}_3$)	[58]
1995	Confirmation via XPS of the Na^+ ion backspillover mechanism of EPOC	[59]
1996	Atomic resolution STM imaging of Electrochemical dosing of Na^+ to Pt catalyst	[60]
1997	First report of EPOC using K^+ conductor (Fe/ $\text{K}_2\text{YZr}(\text{PO}_4)_3$)	[54]
1998	A Monte Carlo simulation of Na of the CO + NO reaction over Pt	[61]
1999	First demonstration of in situ electrochemical control of a base metal catalyst: spectroscopic and kinetic study of the CO + NO Reaction over Na-Promoted Cu	[42]
2001	Rules of chemical promotion	[62]
2001	Application of electron spectroscopy and EPOC to the reduction NO + CO on Rh. Mechanism of alkali promotion in catalysis	[63]
2003	SCR of NO by propene on Pt deposited on NASICON under lean-burn conditions	[53]
2005	Electrochemical promotion by potassium of Rh-catalysed Fischer–Tropsch synthesis at high pressure	[64]
2007	Electrochemical promotion at low temperature (200°C) with (Pt/K- $\beta\text{Al}_2\text{O}_3$). Permanent effect and FTIR-EDX investigation of the promoter phases	[41]
2008	Development of an electrochemically assisted NO_x storage/reduction catalyst on Pt/K- $\beta\text{Al}_2\text{O}_3$ tube. Double role of the alkali ion: promoter and storage component	[65]
2010	In situ regeneration of a Pt catalyst from carbon deposition under fixed conditions by using Na- $\beta\text{Al}_2\text{O}_3$	[66]
2013	Electrochemical promotion of Pt nanoparticles dispersed on a Carbon matrix with K^+ ions	[67]
2014	Bench scale study of electrochemically promoted catalytic CO_2 hydrogenation to renewable fuels on Cu/K- $\beta\text{Al}_2\text{O}_3$	[68]

epoxidation [45], NO reduction [46–48] and hydrogenations [49, 50]. The NASICON family, $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$, another kind of Na^+ ionic conductor was also used for electrochemical promotion studies in ethylene [51] and propylene oxidation [52] and also NO reduction [53]. In 1997, K^+ conductor was used for the first time for NEMCA experiments. Pitselis et al. [54] investigated the decomposition of NH_3 on Fe films deposited on $\text{K}_2\text{YZr}(\text{PO}_4)_3$ and they found an electro-promotional effect at temperatures near 500°C . More recently, de Lucas-Consuegra introduced a different kind of material as a conductor of K^+ ions, K- $\beta\text{-Al}_2\text{O}_3$, to electrochemically promote Pt catalyst on propylene oxidation [41], CO oxidation [55], NO_x [56]

and N_2O reduction [57]. These are only several examples on the great number of studies of alkali electro-promotion. Table 1 summarizes the most relevant contributions along the history of EPOC with alkaline ionic conductors materials as solid electrolytes.

It can be observed that from the pioneering work in 1991 on ethylene oxidation on Pt deposited on $\text{Na-}\beta\text{Al}_2\text{O}_3$ [58] several important contributions have been made in the field from both: fundamental and more applied point of view. Since this first report of alkali electro-promotion, several research efforts have been carried out leading to a thorough understanding of the phenomenon. So far the most important achievement has been the understanding of its origin and mechanism and its contribution to further clarify the effect of alkali promoters in heterogeneous catalysis [62]. The latest progress has been impressive pointing out technological researches in terms of catalyst-electrodes development and its investigation in novel catalytic reaction of environmental and industrial interest [41, 64–68].

3.2 Electrochemical Promotion versus Classical Promotion of Alkali Ions in Heterogeneous Catalysis

As already analyzed in Sect. 2 the chemisorption properties of a metal catalyst can be modified in the same way by the chemical or the electrochemical addition (back-spillover) of alkali ions. For example Lambert and coworkers [59] demonstrated via XPS that the state of Na is the same when it is introduced via evaporation on Pt interfaced with $\text{Na-}\beta\text{Al}_2\text{O}_3$ or via cathodic potential application (through the EPOC phenomenon). A more recent example which shows the same origin and effect of the two ways of promotion has been reported by Pekridis et al. [69]. In this case two different methods of catalyst promotion, were comparatively applied on a catalytic system of significant environmental and practical importance: the N_2O reduction by hydrocarbons (alkanes and alkenes), over Pd catalysts. Results obtained clearly demonstrate the closed similarities that exist between the two methods of promotion, including the response of N_2O and hydrocarbons conversion on K-promotion and reaction conditions. Similar values of the optimum promoter loading were also obtained in both cases [69]. The mode of action of electropositive promoters in conventional, highly dispersed, catalysts have also been recently studied by means of in situ diffuse reflectance infrared Fourier transform spectroscopy [70–72]. Results shown that the addition of alkalis (Na or K) to Pt and Pd based catalyst leads to electron-enriched metal sites, in which the chemisorption bond of electron acceptor adsorbates is enhanced. For instance in Ref. [70], Konsolakis and Yentekakis have analyzed with detail the relative population of adsorbed species formed on the surface of

unpromoted and Na-promoted $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ catalysts, during the NO reduction by propene. It was found that under steady-state reaction conditions the surface of the unpromoted catalyst is mainly covered by carbon containing species, such as hydrocarbon fragments, carboxylates and cyanides. On the opposite, the surface of Na-promoted catalysts is predominantly covered by NO_x adsorbed species, carbonyls and isocyanates, implying the significant effect of Na promoter on surface species formation. The further and clever investigation of the system by IR spectra under different transient atmospheres $\text{NO} \rightarrow \text{He} \rightarrow \text{C}_3\text{H}_6 \rightarrow \text{NO}$ revealed very interesting information regarding the formation of different kind of reaction intermediates on the unpromoted or Na-promoted $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ catalyst. The results showed that over Na-free catalysts the interaction of propene with NO_x pre-adsorbed species (mainly nitrates) leads to the formation of strongly bonded carboxylates and cyanides, which are inactive towards NO. In contrast, NO interaction with the surface of Na-promoted catalysts results in the formation of nitro/nitrite species as well as to nitrosyls, which are highly active towards propene, leading to active intermediates such as isocyanates (NCO). These results clearly explained the strong promotional effect of alkali (Na) dosing to Pt catalyst that have been found in a large number of studies with conventional [18–21] and electrochemical [2, 29, 46, 47, 53] catalyst systems. Then is clear that the unique difference between electrochemical promoting with alkali ions a catalyst surface and the classical promotion (by chemical addition of alkali promoter during the preparation step of the catalyst) is that in the first case one can in situ control the amount of promoter on the catalyst surface. Then the two ways of promotion are equivalent and the unique difference between them is operational and not functional [2]. In fact, the effect of promoters on the overall kinetics of the reaction process only depends on the reaction order of the adsorbates involved in the reaction, their electronic nature (electronegative or electropositive) and the kind of ionic promoters supplied, cations (electropositive promoters) or anions (electronegative promoters). In 2001, simple, rigorous and general rules were developed by Vayenas et al. [62], which described the dependence of catalytic rates on catalyst work function. These rules are in very good agreement with the electrochemical and conventional promotion literature and they are able to predict the rate dependence on work function or promoter concentration on the basis of the rate dependence on the electron donor (D) or electron acceptor (A) reactant partial pressures onto the unpromoted catalyst surface [29]. These rules were progressively established on the basis of experimental observations on electrochemical promotion studies for more than 100 different catalytic systems, using different metals and solid electrolytes [35]. Hence one can

distinguish four main types of global promotional behaviors:

Electrophobic Reactions: Those that show an increase in reaction rate for positive polarization. This type of behavior occurs when the kinetics are positive order in electron donor reactant and zero or negative order in the electron acceptor reactant. Electron donor is more weakly adsorbed on the catalyst surface, and therefore an increase in its chemisorption favors the overall kinetic process.

Electrophilic Reactions: Those that show an increase in reaction rate for negative polarization. This type of behavior occurs when the kinetics are positive order in electron acceptor reactant and zero or negative order in the electron donor reactant. Electron acceptor is more weakly adsorbed on the catalyst surface, and therefore an increase in its chemisorption favors the overall kinetic process.

Volcano-type Reactions: Those that exhibit a maximum in the reaction rate with respect to the applied potential. This type of behavior occurs when both electron donor and acceptor reactants are strongly adsorbed on the catalyst surface.

Inverted Volcano-type Reactions: Those that exhibit a minimum in the reaction rate with respect to the applied potential. This type of behavior occurs when both electron donor and acceptor reactants are weakly adsorbed on the catalyst surface.

Despite of the functional identity and origin between two ways of promotion (chemical and electrochemical) which follow the same general rules the usefulness of the latter is clear. Hence, Table 2 summarizes some of the most important advantages of electrochemical addition of alkali promoters versus its chemical addition to an heterogeneous catalyst. Among the different advantages presented here one of the most interesting one from a fundamental point of view may be the better interpretation of the metal-support interaction effect (MSI) described in literature on conventional dispersed catalysts [73]. It is well established that many supports of heterogeneous catalysts, besides altering physical properties of the catalytic system, such as providing high dispersion and surface area for the catalyst, have also a chemical role in catalysis and are not inert as initially thought. Even when the active phase has the same dispersion or average crystallite size, the support can have a dramatic effect on the catalytic activity or selectivity due to the phenomenon of MSI. Even if the origin of MSI is not fully clarified, recent studies were performed to compare the magnitude of MSI with that of EPOC by using metal-supported catalyst on oxygen ionic conductors such as TiO₂ [74]. These experiments seem to demonstrate that the two phenomena can be explained by a similar process, that is, the backspillover of O²⁻ ionic species from the support onto the metallic particles. These experiments of self-driven EPOC without any electrical polarization demonstrate that

Table 2 Electrochemical promotion (EPOC) versus classical promotion with alkali ions

Advantage	Implications
One can easily control in situ (via potential or current application) the amount of promoter on the catalyst surface	EPOC allows in situ and rapid investigation of the effect of a specific promoter on a catalytic system. EPOC rules allows to interpret the effect of metal-support interactions described in catalysis literature. No need of preparing a number of catalyst with different amount of promoter
One can supply the optimum promoter amount at different reaction conditions	Application in non-stationary processes, e.g., automotive catalysis
One can use the solid electrolyte cell as a “sensor“	It is possible to anticipate the optimum potential conditions which maximize the catalytic rate
One can study the effect of sacrificial promoters with very short life time (O ²⁻ or H ⁺)	This kind of promoters can be hardly studied with conventional catalysts
EPOC could be used to regenerate a catalyst at fixed reaction conditions	With conventional catalyst the reaction conditions must be modified (e.g. regenerating a catalyst from carbon deposition)
Attenuate the effect of poisoning species on catalyst surfaces	Depending on the reaction conditions, the competitive adsorption of poisoning molecules with reactants can be controlled and attenuated
Promote and store compounds on the catalyst surface by the formation of alkaline derived species	This is very important for cyclic processes such as NO _x storage/reduction catalyst (NSR technology for NO _x abatement)

supported dispersed catalysts can also be electropromoted if the support is an ionic conductor. Because O²⁻ backspillover can take place over micrometer distances on the porous Pt films used for EPOC studies with YSZ and TiO₂, it can certainly take place over nanometer distances on the supported Pt nanoparticles of commercial highly dispersed YSZ and TiO₂ supported catalysts. These experiments seem to indicate that the mechanism of MSI promotion of catalytic oxidations can be similar to the mechanism of self-driven electrochemical promotion systems and is based on self-induced migration of promoting O²⁻ species on the nanoparticle catalyst surface. Nevertheless, the EPOC effect allows to control the backspillover of the ionic species and can be reproduced on highly dispersed catalyst which may be of significant importance for the development of more efficient catalyst formulations.

These previous mentioned impact points of EPOC are clear and very interesting from both fundamental and

technological point of view. However, considering that an external electric potential or current are required for the case of EPOC (in contrast with chemical promotion), the reader may ask about the electrical energy consumption for electrochemical promoting a catalyst surface. It has been reported that the cost of the energy to electrochemically supply the promoter ions is lower and typically negligible than other operational costs [2]. This is because a short amount of electrical energy is required, just to supply a low amount of promoter to the catalyst surface. Typical current density values of the order of $\mu\text{A}/\text{cm}^2$ have been reported in literature at catalyst potentials typically below 1 V [41, 53] and maximum power density values required to obtain significant electro-promoted states of $0.5 \text{ mW}/\text{cm}^2$ of catalyst-electrode have been also reported [35]. Considering typical operating conditions of the EPOC studies reported, the energy required for heating the gaseous stream can be estimated around $1.54 \text{ mW}/\text{K}$. In terms of electrical energy, a previous work has reported values of the order of $10^{-3} \text{ J}/\text{cm}^2$ to electrochemically promote a Pt-C catalyst film deposited on K- $\beta\text{Al}_2\text{O}_3$ solid electrolyte [67]. By this way, the permanent EPOC effect observed with cationic solid conductor also allows the saving of additional energy to electrochemically promoted a catalyst as will be analysed below [41]. This permanent effect along with other important recent findings of alkali electro-promotion will be analysed next.

3.3 Recent Findings of Alkali Electro-Promotion in Heterogeneous Catalysis

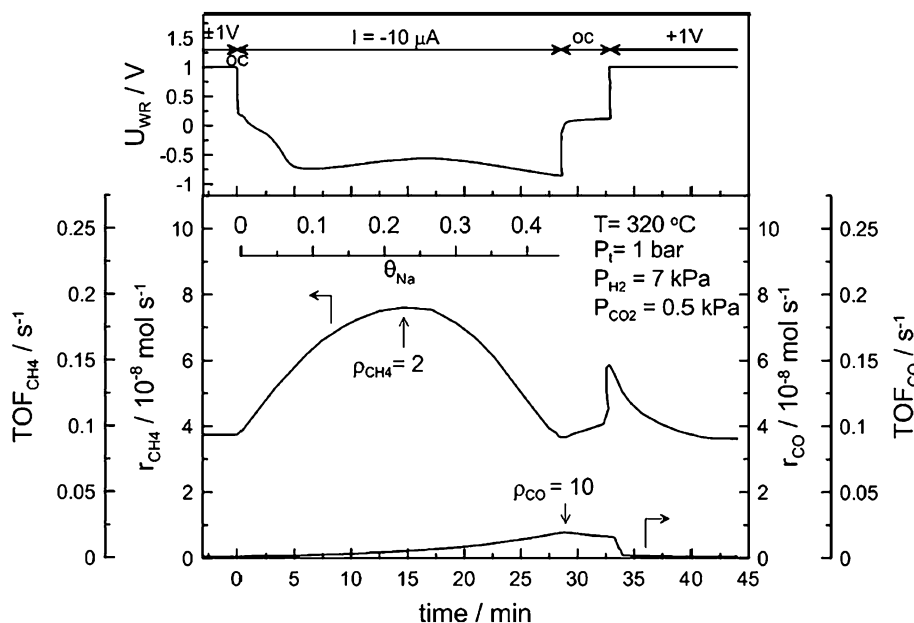
In this section the most relevant recent findings of electrochemical promotion with alkaline ion conductors are analyzed. A recent published experimental data of each demonstrated concept will be shown.

3.3.1 In-Situ Optimization of Alkali Promoter Coverage

As already mentioned in the introduction section of the paper a common feature of most of the previous works of alkali chemical and electrochemical promotion is that the catalytic rate is maximized for a certain alkali content on the catalytic surface [5, 6]. In addition the optimal promoter coverage on the catalyst surface depends on the reaction conditions: the temperature and the reaction mixture composition. This is a direct consequence of the origin of the promotional effect and the competitive chemisorption of reactants at varying reaction conditions. In fact it is well known that the promotional behavior depends on the reaction conditions. For instance, Vernoux et al. [52] showed that for the case of C_3H_6 oxidation reaction on Pt/NASICON near the $\text{C}_3\text{H}_6/\text{O}_2$ stoichiometric

ratio, a strong promotional effect is observed for negative overpotential (electrophilic NEMCA effect) while the opposite trend (electrophobic behaviour), was observed under large excess of O_2 . Hence, authors found an optimum sodium promoter coverage in the Pt catalyst under stoichiometric conditions under application of $\Delta V_{\text{WR}} = -0.2 \text{ V}$, which corresponds to a sodium promoter coverage on the catalyst surface of $\theta_{\text{Na}} = 0.0363$. The possibility of in situ optimize the promoter coverage on the catalyst surface is of relevant importance in a wide variety of catalytic systems, for instance in non stationary process (e.g., automotive catalysis). A previous work demonstrated the possibility of optimizing the behavior of Pt/K- $\beta\text{Al}_2\text{O}_3$ in the selective catalytic reduction of NO_x by C_3H_6 at varying reaction conditions such as those expected for the exhaust of an engine [56]. A more recent example comes from the group of Prof. Vayenas in the hydrogenation of CO_2 over Ru-catalyst electrodes deposited on Na- $\beta\text{Al}_2\text{O}_3$ [75] (experiment of Fig. 3). Figure 3 shows the transient effect of the CO_2 hydrogenation products (CH_4 and CO) under a constant applied current and versus the corresponding Na coverage as well as the catalyst potential response (U_{WR}), at $T = 320 \text{ }^\circ\text{C}$ and $P = 1 \text{ bar}$ under highly reducing conditions ($P_{\text{H}_2}/P_{\text{CO}_2} = 14$, $P_{\text{CO}_2} = 0.5 \text{ kPa}$). It can be observed that the application of a negative current ($I = -10 \mu\text{A}$) promotes the catalytic rates of CH_4 and CO formation. Although the rate of CO production increases monotonically with the Na promoter coverage, the rate of CH_4 formation firstly increases and then it decreases after a certain coverage of sodium ($\theta_{\text{Na}} = 0.23$) is achieved. Then this coverage of promoter allows to optimize the CH_4 formation according to the kinetic order of the reactants molecules at the explored conditions. Other experiments carried out in the same study [75] (not shown here) showed that upon increasing the partial pressure of CO_2 to 3 kPa at atmospheric pressure, the maximum rate of CH_4 formation was strongly suppressed and displaced to lower Na^+ coverage (0.05 instead of 0.23), because, in this case, the methanation rate is near to zero order in CO_2 . Upon increasing the pressure to five bar the rate of CO formation vanishes and CH_4 was the unique product. Under those conditions, the maximum rate shifted to higher Na coverage levels ($\theta_{\text{Na}} = 0.15$). Therefore it is clear that the EPOC phenomena allows to rapidly explore and supply the optimum promoter amount at different reaction conditions. This is not possible in conventional catalytic promotion (chemical) where each catalyst has a fixed amount of promoter. One can find in literature other similar recent examples in a wide variety of catalytic systems such as the steam reforming and partial oxidation of methanol [67], water gas shift reaction [76], or ethylene epoxidation [45], etc.

Fig. 3 The transient effect of a constant applied current and corresponding Na coverage on rates of CH₄ and CO formation on Ru/β⁻-Al₂O₃ and on the catalyst potential U_{WR}. P_t = 1 bar, P_{H₂} = 7 kPa; P_{CO₂} = 0.5 kPa, T = 320 °C. Reprinted with permission from Ref. [75]



3.3.2 Electrochemical Activation of a Metal Catalyst at Lower Reaction Temperatures

The activation of metal catalyst at lower reaction temperatures has a great technological importance especially in environmental catalysis. For example in the treatment of car exhaust engine emissions where most of the pollutant emissions occur during the cold start engine regime. A previous work of de Lucas-Consuegra et al. studied CO oxidation activities on Pt/K-βAl₂O₃ electrochemical catalyst through temperature-programmed reaction experiments (light-off measurements) under application of five different catalyst potentials [55]. Results obtained showed that as the catalyst potential decreased to lower values (electrochemically supplying K⁺ ions to the Pt catalyst) the activity of the catalyst began at lower reaction temperatures. For example under application of -2 V, the value of the light off temperature (Temperature at which the catalyst achieved 50 % of conversion) dropped by almost 40 °C in comparison to the un-promoted Pt catalyst (under application of 2 V). Another important point is that the temperature corresponding to the beginning of the catalytic activity (5 % of CO conversion) decreased from about 240 °C without promoters (+2 V) to 210 °C in the presence K⁺ cations (-2 V). Recently a similar example have been reported for the selective catalytic reduction of N₂O by C₃H₆ also using a Pt/K-βAl₂O₃ electrochemical catalyst [57]. The SCR activity of the system was also investigated through temperature-programmed reaction experiments (light-off measurements) under application of four different catalyst potentials (Fig. 4). Experiments were carried out at a fixed gas composition of C₃H₆/N₂O/O₂: 2,000/

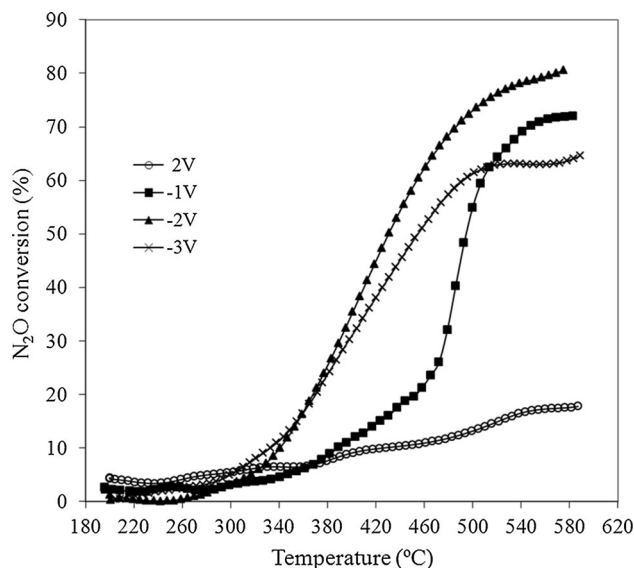


Fig. 4 N₂O conversion versus the reaction temperature at different catalyst potential on Pt-KβAl₂O₃. Conditions: C₃H₆/N₂O/O₂: 2,000 ppm/1,000 ppm/2,000 ppm, He balance. Reprinted with permission from Ref. [57]. Copyright 2014 Elsevier

1,000/2,000 ppm between 200 and 600 °C with a constant heating rate of 2 °C/min. It can be observed, that as the catalyst potential decreased, the system could be strongly promoted above 340 °C. While in the case of unpromoted catalyst (V_{WR} = 2 V) the N₂O conversion did not exceed 17 % at high temperatures (580 °C), the electrochemically promoted ones (V_{WR} < 2 V) exhibited higher conversions at much lower temperatures. For instance, for an applied catalyst potential of V_{WR} = -2 V (which allowed to

supply the optimal promoter coverage for the explored reaction conditions), the temperature corresponding to 15 % of N_2O conversion (T_{15}) decreased by 167 °C in comparison to the unpromoted catalyst ($V_{\text{WR}} = 2$ V). These results demonstrate the interest of EPOC for activating a catalyst at lower reaction temperatures which may also have strong importance for reactor energy savings in industrial processes.

3.3.3 Enhancement of Catalytic Selectivity

One of the most promising features of alkali-electropromotion is related to product selectivity modification and a great number of examples can be found in literature. Particularly interesting is the case of the selective catalytic reduction of NO_x , where the production of N_2 instead of N_2O (a greenhouse effect gas) is one of the key aspects for the design of effective catalyst that allows to reduce pollutants concentration in future legislation. For instance Vernoux et al. [53] studied the SCR of NO_x on Pt deposited on NASICON under real oxidizing conditions. They found an increase in the N_2 selectivity at 295 °C from 30 to 65 % under cathodic potential application (electrochemically supplying Na^+ ions to the Pt catalyst). Similar results have also been reported on the SCR of NO_x under similar oxidizing conditions and lower reaction temperatures on Pt/ $\text{Na}-\beta\text{Al}_2\text{O}_3$. In this work N_2 selectivity was increased from 20 to 45 % under Pt modified by Na^+ surface [47]. Even under wet reaction conditions and large excess of Oxygen (more representative conditions from a real exhaust of a car engine), the N_2 selectivity was increased from 40 to almost 100 % of N_2 selectivity on Pt/ $\text{K}-\beta\text{Al}_2\text{O}_3$ electrochemical catalyst [56]. A similar electro-promotional effect has been reported in the SCR of NO_x for a wide range of reaction conditions and reductant agents such as CO [44, 48], ethylene [59] and even by using non noble metal catalysts such as Cu [42]. The importance of Electrochemical Promotion with alkali ions in catalyst selectivity has also been widely investigated and demonstrated in other catalytic process of great industrial interest. For instance in the Selective Hydrogenation of Acetylene [77], Fischer-Tropsch synthesis [64] or CO_2 hydrogenation [75]. A more recent and impressive example can be found on Ref. [68] for the synthesis of fuels by CO_2 hydrogenation on Cu deposited on $\text{K}-\beta\text{Al}_2\text{O}_3$ (at bench scale). Figure 5 shows the effect of the response of CO_2 conversion and selectivity to CH_3OH , $\text{C}_2\text{H}_5\text{OH}$ and $\text{C}_2\text{H}_6\text{O}$ to different applied potentials (between 4 and -2 V). Experiments were carried out at 325 °C and using a H_2/CO_2 ratio of 3. It can be observed that the CO_2 hydrogenation is significantly affected by the applied potential, with selectivity to CH_3OH , $\text{C}_2\text{H}_5\text{OH}$ and $\text{C}_2\text{H}_6\text{O}$ enhanced up to 27.7, 27.9 and 47.1 %, respectively, under optimal potential conditions

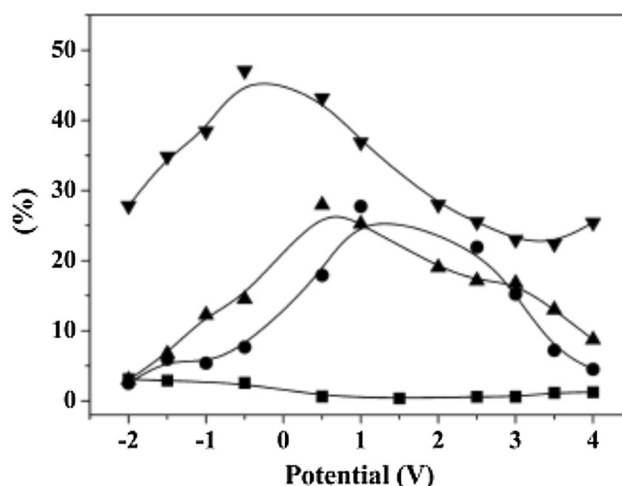


Fig. 5 The influence of the applied potential on (closed square) CO_2 conversion and on selectivity to (closed circle) CH_3OH , (closed triangle) $\text{C}_2\text{H}_5\text{OH}$ and (closed inverted triangle) $\text{C}_2\text{H}_6\text{O}$, ($\text{H}_2/\text{CO}_2 = 3$, $T = 325$ °C) on Cu- $\text{K}\beta\text{Al}_2\text{O}_3$. Reprinted with permission from Ref. [68]. Copyright 2014 Elsevier

(optimal potassium coverage on the Cu catalyst). These results demonstrate the interest of EPOC with cationic conductors materials in this case for the production of different target fuels whose selectivity can be modulated by modifying applied potential under given operating conditions. Its application in other catalytic fields, for example in fine chemistry, may open novel opportunities for the improvement of catalytic processes.

3.3.4 Permanent Electrochemical Promotion

The permanent EPOC effect is one of the most interesting and potentially important characteristics of the electrochemical promotion from a practical point of view [2]. It allows to keep the electro-promotional effect on the catalytic system upon current interruption (under open circuit conditions). By this way an initial polarization is only required to electrochemically supply promoter ions which allows to reduce electrical energy requirements, polarizing the catalyst only for a short period of time. This permanent EPOC effect was firstly discovered by Comminellis for the case of (O^{2-}) conductors [78] and latter it has also been reported for the case of K^+ conductor materials [41, 79]. Hence, for the case of alkali electro-promotion the origin of this phenomenon has been explained considering the stability of the promoter species formed by the electrochemical supplied ions and the co-adsorbed reactants molecules. Hence, as already demonstrated with different in situ and ex situ characterization techniques, the electrochemically supplied promoting ions under EPOC reaction conditions form surface compounds with the different chemisorbed

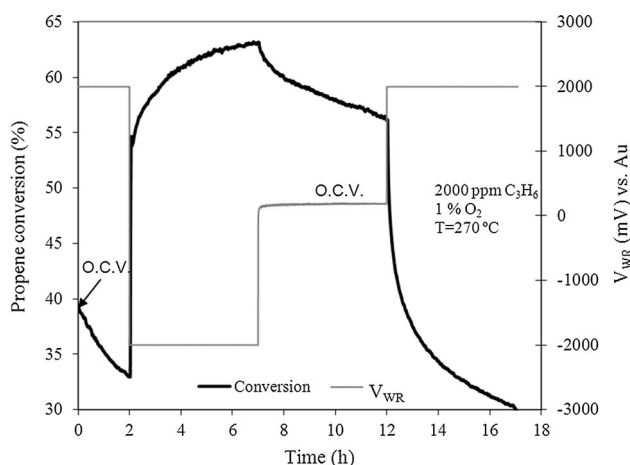


Fig. 6 Propene conversion response versus time to step changes in applied catalyst potential: 2,000 ppm C_3H_6 , 1 % O_2 , $T = 270\text{ }^\circ\text{C}$ on Pt-K β Al $_2$ O $_3$. Reprinted with permission from Ref. [41]. Copyright 2014 Elsevier

reactants molecules under reaction conditions [42, 52, 56, 63, 65, 80]. Resultant promotional phases some times are very stable and remain in the catalyst surface even under open circuit potential conditions. For instance Fig. 6 shows an example of the permanent EPOC effect for the case of propene oxidation reaction with Pt/K- β Al $_2$ O $_3$ electrochemical catalyst under C_3H_6/O_2 : 2,000 ppm/1 % at 270 °C [41]. This experiment depicts the response of the propene conversion versus time to step changes in applied potential. Apart from the strong promotional effect observed during the negative potential application of -2 V , the most important point of this experiment is that after the negative polarization, at $t = 7\text{ h}$, under open circuit conditions (O.C.V.), the catalyst showed just a slight decrease on its catalytic activity. Indeed, after 5 h, the propene conversion decrease was lower than ten points. The investigation by a variety of in situ (cyclic voltammetry, FTIR) and ex situ techniques (SEM-EDX) have shown strong evidences that the permanent NEMCA effect was due to the electrochemical creation and stabilization of promoter oxides and superoxides on the catalyst surface such as potassium oxides and peroxides [41]. These kind of species are formed on the catalyst surface during the negative polarization step and are stable under open circuit conditions leading to the observed permanent effect.

3.3.5 Electrochemical Storage of Surface Compounds

The possibility of electrochemical store surface compounds on a porous catalyst film via electrochemical supply of alkali ions has opened a novel application of cationic electrochemical catalyst. Hence the possibility of

store large amount of surface compounds was firstly reported by de Lucas-Consuegra et al. [65]. In this previous work a tubular Pt/K- β Al $_2$ O $_3$ electrochemical cell was used as NO_x storage/reduction catalyst that can operate over a range of reaction conditions for the effective removal of NO_x . In the first step under negative polarization (electrochemical pumping of potassium ions), NO_x was stored on the catalyst surface in form of potassium nitrates. In this initial step potassium ions electrochemically transferred to the Pt catalyst have a double role in the NSR process: as a promoter for the NO oxidation reaction and as storing sites by the formation of potassium nitrates. In a second step, under positive polarization the catalyst was regenerated, and stored nitrates were efficiently desorbed and reduced to N_2 . The variation of the current under the applied polarizations allowed monitoring the progress of both: storing and regeneration phases, and therefore to optimize the duration of both sequences in a feasible technical way. Moreover, the possibility of electrochemical regeneration of the catalyst surface allowed to work under a fixed lean gas composition, which implies an important technological advance for the NSR process [81]. A more recent example on the use of a cationic electrochemical catalyst to store and remove pollutants has also been developed by Ruiz et al. for the case of CO_2 capture [82]. In this research, authors reported a bench-scale study of the electropromoted CO_2 capture over Pt on K- β Al $_2$ O $_3$, at high flow rate and using simplified exhaust gas compositions (CO_2/N_2 and $CO_2/O_2/N_2$). Hence Fig. 7, shows the response of current density (j) and CO_2 concentration versus time (t) and potential (E) during an anodic voltammetry (catalyst regeneration at 400 °C), after an adsorption step at -1 V in the presence of CO_2 (12.6 %) and O_2 (5.3 %) at 400 °C. As can be observed on this figure, two anodic (positive) current peaks were obtained during the voltammetry. It seems evident that the sharper peak at 1.8 V, which coincides with the maximum in released CO_2 , corresponds to decomposition of potassium carbonate species previously stored during negative polarization. Therefore, it seems to confirm the possibility of monitoring the decomposition of captured compounds by a simple electrical measurement without the experimental analysis of the exiting CO_2 content. The overall amount of stored CO_2 calculated from the experiment of Fig. 7 was around 1,130 mg CO_2/g Pt. Additionally the authors reported that CO_2 capture is enhanced on decreasing Pt particle size, in the presence of O_2 and at higher temperatures up to a certain value which depends on the thermal stability of the species formed. The Pt/K- β Al $_2$ O $_3$ system can be regenerated, allowing CO_2 separation, by electro-chemical decomposition of previously stored compounds without increasing temperature.

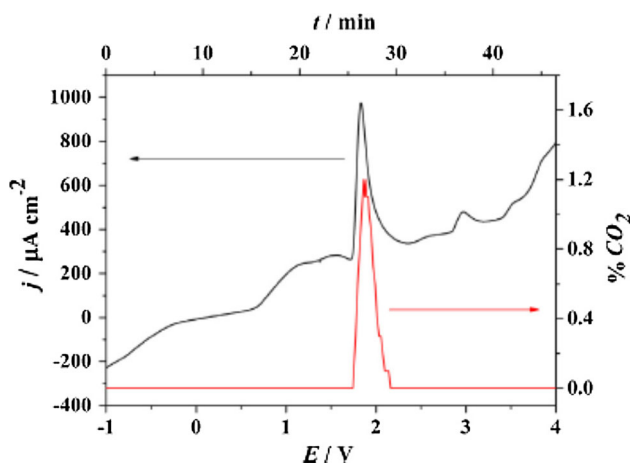


Fig. 7 CO_2 concentration and current density variation (j) versus the applied potential/time during linear voltammetry in N_2 at 400°C over electrocatalyst Pt/K- $\beta\text{Al}_2\text{O}_3$. Adsorption step at -1 V in the presence of CO_2 (12.6 %) and O_2 (5.3 %) at 400°C . Reprinted with permission from Ref. [82]. Copyright 2014 Elsevier

3.3.6 In Situ Electrochemical Regeneration of a Deactivated Catalyst at Fixed Conditions

One of the typical common limitations of heterogeneous catalyst is its deactivation by carbon deposition for instance in hydrocarbon reforming and partial oxidation reactions. It leads to a progressive decrease in a number of catalytic active sites with the consequent deactivation of the catalyst. Thus, current intense research efforts are being placed to develop new catalyst configurations, which are able to overcome the above mentioned limitations for on-board H_2 production from methane. In a recent work [66] a new electrochemical catalyst (Pt-Pt/YSZ/Na- $\beta\text{Al}_2\text{O}_3$) has been prepared and characterized for the H_2 production at low temperature from CH_4 with a high CO_2 selectivity. It has been tested under Electrochemical Promotion conditions under different reaction systems: steam reforming, partial oxidation and autothermal steam reforming. Among them, the latest system seems to be the most suitable one for the operation of the electrochemical catalyst in a cyclical way between positive and negative polarizations. Hence, Fig. 8 shows an example on the mode of operation of the electrochemical catalyst. This figure shows the variation of H_2 , CO and CO_2 production rates with time on stream under different cycles of positive and negative potentials under ATR conditions ($\text{CH}_4/\text{H}_2\text{O}/\text{O}_2$: 1%/4//0.2%, N_2 balance at 500°C). In this experiment, a negative potential of -1 V was applied for 4 h and then a positive polarization of 2 V was applied for 2 h. It can be observed that under positive polarization, the electrochemical catalyst produced a high amount of H_2 however a strong deactivation was also observed due to the deposition of carbon. Upon the application of this positive potential increased the chemisorption

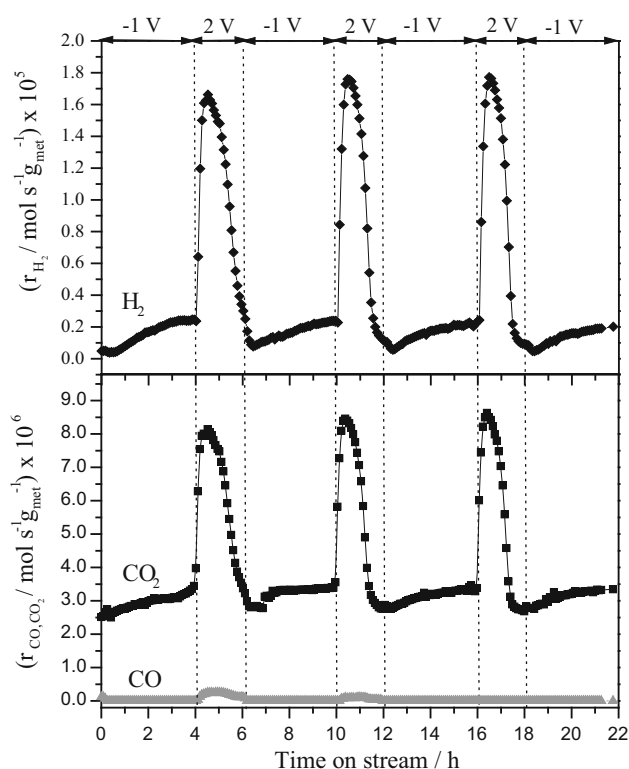


Fig. 8 The Influence of the applied potential on H_2 , CO and CO_2 production rates during the reproducibility experiment under ATR conditions ($\text{CH}_4/\text{H}_2\text{O}/\text{O}_2$: 1/4/0.2 %) at 500°C on on Pt-Pt/YSZ- $\text{Na}\beta\text{Al}_2\text{O}_3$. Reprinted with permission from ref [66]. Copyright 2014 Elsevier

of CH_x -species was increased, enhancing the production of H_2 but leading to a fast deactivation due to the low coverage of water and oxygen molecules responsible from the removal of carbon. Nevertheless, the subsequent application of negative polarization leads to a strong increase in the coverage of O_2 and H_2O , electron acceptor molecules (induced by the electrochemical supply of Na^+ ions) that caused the removal of the deposited carbon and, hence, the regeneration of the catalyst. This system showed a reproducible behaviour along different cycles demonstrating that the phenomenon of electrochemical promotion with alkali ionic conductors could be used to regenerate, in an unlimited way, the catalytic performance of the system for the low temperature H_2 production from CH_4 . In addition, this catalyst regeneration could be carried out under fixed reaction conditions, which would avoid the requirement of modifying the reaction atmosphere in contrast with conventional catalytic systems.

4 Conclusions and Prospects

Electronic promoters such as alkali ions play a key role in the improvement and development of novel catalyst

configurations. Thus, upon adding promoters on the catalyst surface (chemically or electrochemically), the chemisorptive bond strength of reactants and intermediates is modified and the catalytic kinetic is usually changed dramatically.

The possibility of in situ control the alkali promoter coverage on the catalyst surface under working conditions through the EPOC concept opens new opportunities in the field of heterogeneous catalysis. Related to environmental catalysis, the optimization of the catalytic activity at varying reaction conditions or the activation of metal catalyst at lower reaction temperatures are of great technological importance especially in the treatment of car exhaust engine emissions. The improvement of catalytic selectivity, the possibility of regenerating a catalyst at fixed reaction conditions or the electrochemically assisted synthesis of renewable fuels from CO₂ could also have a strong importance in fine chemistry and in large scale industrial catalytic processes.

The phenomenon of Electrochemical Promotion has completely opened a new research field to explore novel alternatives in order to improve chemical and environmental industrial processes in the future. The technological progress of this phenomenon has to be focused on finding new industrial and environmental reactions and new ways of operating catalytic systems. It is also challenging to investigate EPOC in potential catalytic reactions with a non well established market in order to assist the technology entrance. In addition, further fundamental studies should be done to extend chances for EPOC commercial applications. The multidisciplinary approach of EPOC combining heterogeneous catalysis, solid state electrochemistry and materials science has certainly contributed to the wide utilization of ionically conducting ceramics in catalysis. The understanding of the interactions of metallic active sites and ionically conducting support through the EPOC phenomenon may contribute with no doubt to the development of more efficient catalysts formulations. Moreover, the development of new materials: solid electrolytes of higher ionic conductivities at lower temperatures, and new catalyst-electrodes of higher catalytic activity could be a good contribution to broaden applications of this phenomenon.

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