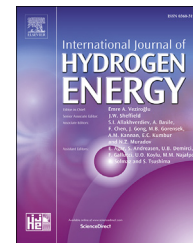


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## Electrochemical vs. chemical promotion in the H<sub>2</sub> production catalytic reactions

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### ABSTRACT

The addition of electronic promoters chemically (chemical promotion) or electrochemically (electrochemical promotion or EPOC) induces very significant and similar effects on catalytic hydrogen production reactions such as CH<sub>4</sub> and CH<sub>3</sub>OH conversion reactions, water-gas shift or ammonia decomposition. Both kinds of promotional phenomena follow the same general mechanism but the usefulness of the latter is highlighted. In this paper, the most important and recent contributions of the electrochemical promotion in different hydrogen production reactions are reviewed and compared to those based on conventional chemical promotion methods, mostly focusing on alkali promoters. The functional similarities and operational differences between both promotion ways are pointed out, and their impact on the hydrogen production technology is discussed. By this way the possibility of in-situ controlling the promoter coverage on the catalyst under working conditions and the in-situ catalyst regeneration from carbon deposition, among other novel contributions, lead EPOC to new opportunities for both: development of tailored effective catalysts and operation of hydrogen catalytic processes.

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### Introduction

Hydrogen is a very important feedstock in the chemical industry and a promising energy carrier with main application in internal combustion engines and in fuel cell technology, as clean and efficient alternative to the massive consumption of fossil fuels [1–4]. There are many possible ways to produce hydrogen. For instance, it can be obtained from electro-oxidation of water [5–7] or alcohols [8–11], biomass thermochemical conversion processes [12,13] or photocatalytic water splitting [13,14]. However, H<sub>2</sub> is mainly obtained from catalytic steam reforming of methane [15–17] due to its advanced

technological development degree, the high availability of the feedstock and its high H/C ratio. Other methane conversion reactions for H<sub>2</sub> production are the partial oxidation, the autothermal reforming (i.e., with both O<sub>2</sub> and H<sub>2</sub>O) and the dry reforming (i.e., with CO<sub>2</sub>). All these reactions are typically catalysed by nickel or noble metals (e.g. Pt or Rh) supported on different metal oxides [15,16], and are usually followed by additional H<sub>2</sub> purification steps through preferential oxidation of CO or water-gas shift reaction [18]. The use of liquid hydrogen carriers such as alcohols is also acquiring increasing interest mainly due its easier transport, handle and storage at ambient conditions. For instance, hydrogen may be obtained from decomposition, steam reforming or partial oxidation of

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methanol by using catalysts based on Cu or groups 8–10 metals [16,19,20]. The main difficulties found when carrying out catalytic reactions for H<sub>2</sub> production from carbon feedstocks are related to metal particles sintering and catalyst deactivation by carbon deposition or sulphur poisoning. Hence, a high catalytic activity, a low CO selectivity and a high stability of the catalyst are always the main targets. In order to improve the behaviour of these catalysts two kinds of promoters have been widely studied in literature: structural and electronic ones. The use of structural promoters such as metal oxide supports, e.g. Al<sub>2</sub>O<sub>3</sub> or CeO<sub>2</sub> [15,16,19,20], allows to improve the dispersion and the catalyst stability against sintering of the active phase. On the other hand, the use of electronic promoters allows to enhance the catalytic properties of the active phase itself, for instance by using alkali dopants [21,22]. This second kind of promotion is of great scientific and technological important since it allows to introduce several achievements on the catalytic performance, as well as to overcome some of the typical limitations in catalytic H<sub>2</sub> production processes such as the low catalytic selectivity and the carbon deposition in reforming reactions [23–29]. The doping of heterogeneous catalysts with electronic promoters, also known as chemical, classical or conventional promotion, is typically carried out by the chemical addition of oxide or hydroxide compounds onto the catalyst support together with the active phase. In this way, one can highlight the recent studies on methanol steam reforming and water-gas shift (WGS) reactions carried out by the groups of prof. Wasserscheid [30–32] and Davis [33–36], where different Pt-based catalysts were doped by alkali metals such as Li, Na or K. These chemical promoters are typically added during the

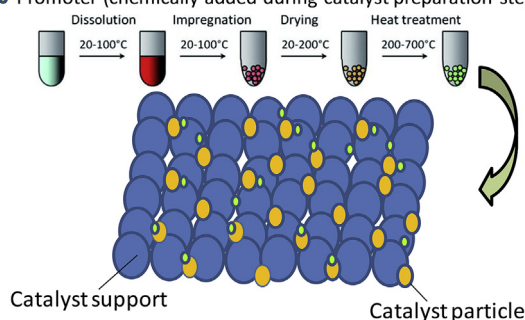
catalysts preparation steps (e.g. by the incipient wetness impregnation method) as schematized in Fig. 1a. In this case, the promoter coverage on the active phase cannot be exactly controlled since part of the promoter is deposited on catalytically inert support areas. In addition, the amount of promoter is fixed before catalyst exposure to reaction conditions and it cannot be modified afterwards.

In the last years a new tool has been developed for introducing chemical promoters on catalyst surfaces through the use of solid electrolytes as electro-active catalyst supports by the phenomenon of electrochemical promotion of catalysis (EPOC). In this case, the coupling of catalysis and electrochemistry has opened a new way to promote and improve the catalytic activity/selectivity of catalysts under working reaction conditions [37]. This technique consists of the electrochemical pumping of promoter ions to a catalyst film from the electro-active catalyst support which is a solid electrolyte material (Fig. 1b). For example, in the case of alkaline solid electrolyte materials (e.g., Na<sup>+</sup>- or K<sup>+</sup>- conductor) the application of a cathodic polarization (negative electric polarization) between the catalyst-working electrode and an inert counter electrode deposited at the opposite side of the solid electrolyte induces the migration (back-spillover) of the promoter ions to the catalyst film. Hence, the electrochemical potential driving force allows to modify the promoter coverage directly on the active phase in a reversible and controllable way [37,38]. However, it should be mentioned that the origin and fundamentals of this way of promotion (EPOC) is essentially the same as the origin of the chemical promotion in heterogeneous catalysis which consists on the modification of the chemisorption properties of the catalyst in the presence of the electronic promoter [39]. In fact, both kinds of promotion methods, chemical and electrochemical, are functionally identical and only operationally different [37]. In contrast to chemical promotion, the electrochemical promotion allows the in-situ modification of the promoter amount under working reaction conditions. Such an advantageous feature of EPOC vs. chemical promotion has been applied in the past in numerous catalytic reactions as reviewed in detail elsewhere [37,40]. For instance, chemical and electrochemical promotion mechanisms by sodium have been extensively compared for NO reduction by hydrocarbons [41,42]. Concerning the H<sub>2</sub> production reactions, Tsiplakides and Balomenou [43] critically analysed the key role that the EPOC concept could play in this field. In this way, the EPOC phenomena has been applied in some of the most important H<sub>2</sub> production reactions such as methane [44–46] and methanol [47–53] conversion via steam reforming and partial oxidation reactions, the water-gas shift process [54,55] and ammonia [56] decomposition reactions. In these studies different metal catalysts and solid electrolyte materials (ionic conductors) were employed as summarized in Table 1. This table also shows the maximum hydrogen production rate enhancement ratio (induced by EPOC) reported in each work.

The aim of this paper is to review and describe some of these previous works showing the most relevant achievements in the field. In this way we tend to analyse the common features between chemical and electrochemical promotion of catalysis in hydrogen production reactions in order to bring closer this novel and fascinating phenomenon to the catalysis

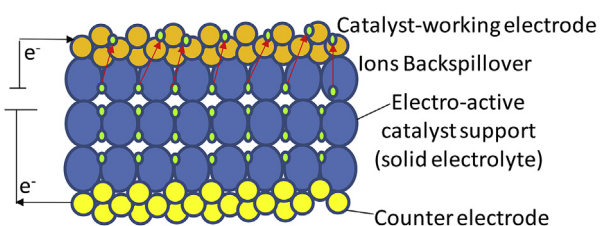
### (a) Chemical promotion

- Promoter (chemically added during catalyst preparation step)



### (b) Electrochemical promotion

- Promoter ions (electrochemically supplied under reaction conditions)



**Fig. 1** – Schematic illustration of catalyst doping procedures by (a) chemical and (b) electrochemical promotion.

**Table 1 – Electrochemical Promotion studies published in literature on H<sub>2</sub> production catalytic reactions.**

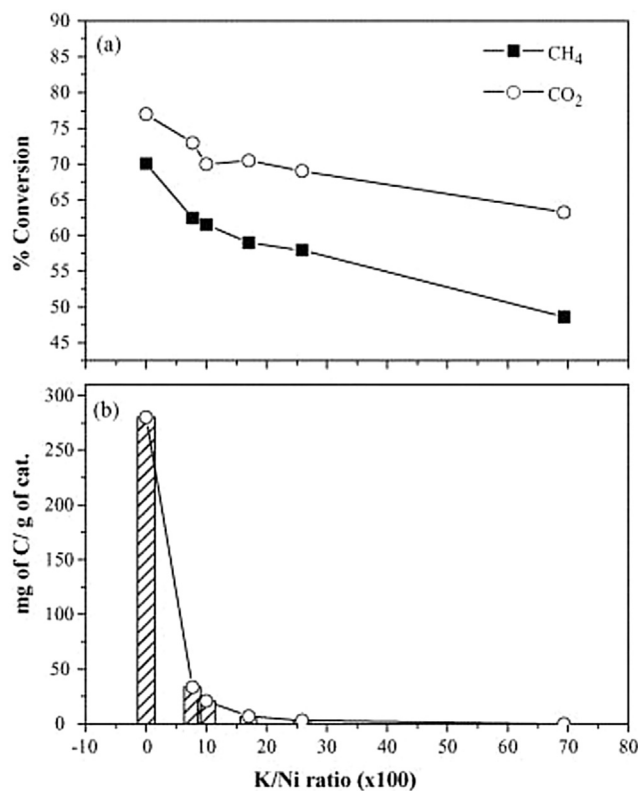
Reactants	Gaseous products	Solid electrolyte	Catalyst	Maximum H <sub>2</sub> production rate enhancement ratio	Ref.
CH <sub>4</sub> , H <sub>2</sub> O	H <sub>2</sub> , CO, CO <sub>2</sub>	YSZ	Ni	2	[44]
			Pt-YSZ	4	[45]
CH <sub>4</sub> , H <sub>2</sub> O, O <sub>2</sub>	H <sub>2</sub> , CO, CO <sub>2</sub>	Na-βAl <sub>2</sub> O <sub>3</sub>	Pt-YSZ	∞ (regeneration of deactivated catalyst)	[46]
CH <sub>3</sub> OH	H <sub>2</sub> , CO, H <sub>2</sub> CO, CH <sub>4</sub>	K-βAl <sub>2</sub> O <sub>3</sub>	Ni	5	[47]
		YSZ	Ag	Not quantified	[48]
CH <sub>3</sub> OH, H <sub>2</sub> O	H <sub>2</sub> , CO, CO <sub>2</sub>	K-βAl <sub>2</sub> O <sub>3</sub>	Ni	2	[47]
			Pt	5	[49]
CH <sub>3</sub> OH, O <sub>2</sub>	H <sub>2</sub> , CO, CO <sub>2</sub> , H <sub>2</sub> CO, HCOOCH <sub>3</sub>	K-βAl <sub>2</sub> O <sub>3</sub>	Pt	6	[50]
			Ni-C	2	[51]
			Au-YSZ	9	[52]
			Cu	3	[53]
CO, H <sub>2</sub> O	H <sub>2</sub> , CO <sub>2</sub>	YSZ	Pt	3	[54]
		K-βAl <sub>2</sub> O <sub>3</sub>	Ni	3	[55]
NH <sub>3</sub>	H <sub>2</sub> , N <sub>2</sub>	K <sub>2</sub> YZr(PO <sub>4</sub> ) <sub>3</sub>	Fe	<2	[56]

scientific community, specially into the hydrogen production field.

### Chemical and electrochemical promotion of CH<sub>4</sub> conversion reactions

Catalysts employed in methane conversion reactions for H<sub>2</sub> production (e.g., steam reforming, autothermal reforming or dry reforming) are typically based on nickel [16] supported on Al<sub>2</sub>O<sub>3</sub> and/or other oxides of transition metals (e.g. Zr) and rare earth elements (e.g. Ce, La), thus improving the dispersion and stability of the Ni particles [24–27,57]. As mentioned below, alkali and alkaline-earth promoters are also commonly used to improve the activity and/or selectivity of reforming catalysts [15,16]. A typical preparation method consists of the impregnation of the catalyst support with an aqueous solution of metal precursors such as nitrates [23–25,27]. For instance, a common promoter is MgO which has shown to enhance the catalytic activity in the different CH<sub>4</sub> conversion reactions since its presence causes water adsorption activation [16,23,26]. On the other hand, in the steam reforming of mixtures of CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>, chemical promotion with potassium increases the catalyst selectivity toward the reforming of the former [58,59]. However, potassium addition usually causes the decrease of the overall methane conversion due to the blockage of catalyst active sites [23–27,58,59]. It is important to note that in all cases the stability of the catalysts is enhanced by the addition of alkali and alkaline-earth metals [23–27,58,59]. This kind of promoters is of particular interest in the case of Ni-based catalysts, which are especially prone to deactivation by deposition of carbon fibres or filaments [16,60]. In the presence of steam, i.e., in methane steam reforming and autothermal reforming, the increase in the catalyst stability is mainly attributed to the strengthening of water chemisorption on the catalyst surface and, thus, to the promotion of the gasification of the carbonaceous species [23,24,58,59]. Furthermore, the suppression of carbon deposition is observed even in methane dry reforming (with CO<sub>2</sub>) over K-promoted catalysts, due to the fact that alkali promoters firstly block the most active sites responsible for both

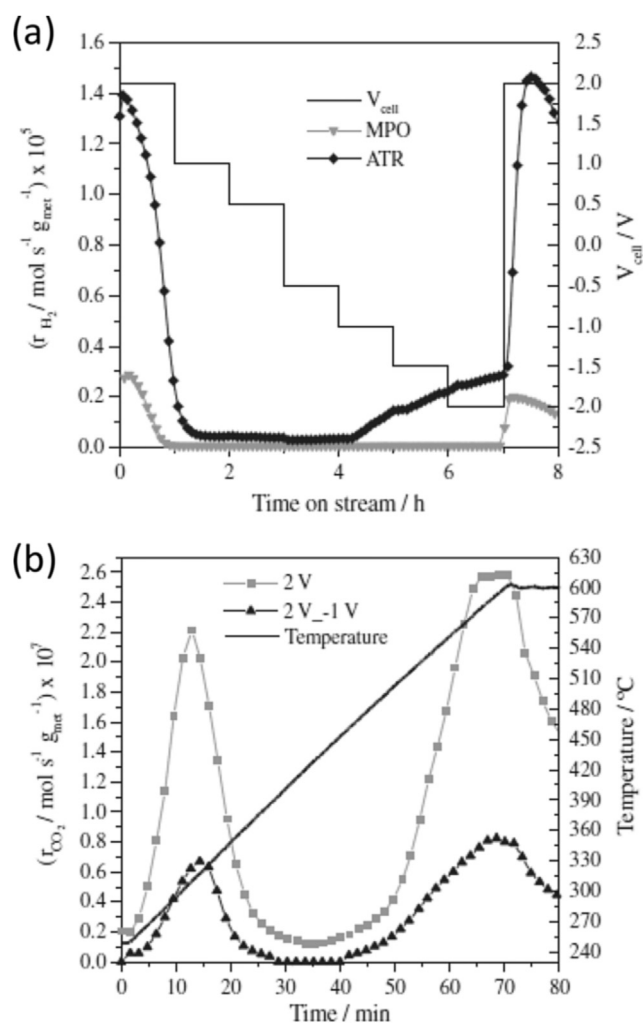
methane reaction and carbon deposition [25,27]. For instance, Fig. 2 (directly obtained from Ref. [25]) shows the influence of potassium loading on the catalytic activity of a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst in methane dry reforming (Fig. 2a) and on the carbon deposition (Fig. 2b). It is clear that the addition of fairly low amounts of K<sub>2</sub>O (c.a. 0.2 wt.%) did not significantly reduce the methane conversion while it caused a sharp decrease in the



**Fig. 2 – Effect of K/Ni ratio on (a) steady-state CO<sub>2</sub> and CH<sub>4</sub> conversion and (b) amount of coke deposited after 6 h reaction at 700 °C. Catalysts: Ni/Al<sub>2</sub>O<sub>3</sub> doped with K<sub>2</sub>O (0–5 wt.%). Methane dry reforming conditions: CH<sub>4</sub>/CO<sub>2</sub> composition of 50%/50%, space velocity of 22500 h<sup>-1</sup>. Reprinted with permission from Ref. [25].**

formation of carbon deposits which leads to a better catalyst stability.

One can find in literature an equivalent promotional effect in alkali electrochemically promoted catalysts. In this case the possibility of in-situ controlling the amount of alkali promoter on the catalyst allows not only the prevention of the catalyst deactivation by carbon deposition during methane reforming reactions, but also the catalyst activation and regeneration in the course of the catalytic reaction, as previously reported by our group [46]. In this study it was shown that a Pt-based catalyst film, which also behaved as working electrode, was electro-promoted under different methane reaction atmospheres by the electrochemical supply of  $\text{Na}^+$  ions from the  $\text{Na-}\beta\text{Al}_2\text{O}_3$  electroactive catalyst support (i.e.,  $\text{Na}^+$  conductor).

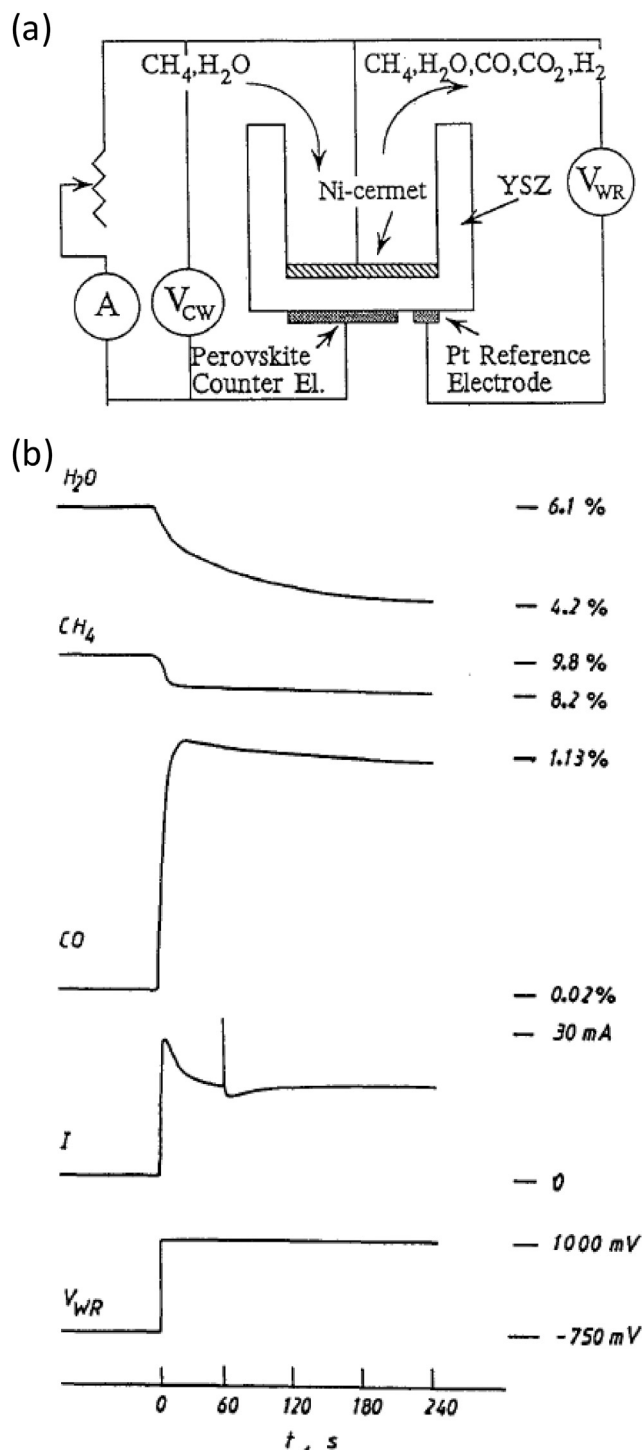


**Fig. 3** – (a) Dynamic response of  $\text{H}_2$  production rate to step changes in applied electric potential ( $V_{\text{cell}}$ ) under methane autothermal reforming (ATR,  $\text{CH}_4/\text{H}_2\text{O}/\text{O}_2$  composition of 1%/4%/0.2%) and methane partial oxidation (MPO,  $\text{CH}_4/\text{O}_2$  composition of 1%/0.2%) conditions at 500 °C. Catalyst: Pt-YSZ/ $\text{Na-}\beta\text{Al}_2\text{O}_3$  ( $\text{Na}^+$  ions conductor). (b) TPO analysis of catalyst after exposure to ATR conditions and two different polarization sequences: application of +2 V (4 h); and application of +2 V followed by –1 V (4 h each). Reprinted with permission from Ref. [46].

Fig. 3a shows the variation of the  $\text{H}_2$  production rate from methane partial oxidation (denoted as MPO) and autothermal reforming (denoted as ATR) under different applied potentials ( $V_{\text{WR}}$ ) between the Pt catalyst-working electrode and the Au counter electrode located in opposite sides of the solid electrolyte (as previously shown on Fig. 1b). In this kind of electrochemical promotion studies that use alkaline conductors (such as  $\text{K}^+$ - or  $\text{Na}^+$ -conducting supports), a positive potential (e.g. +2 V) is usually applied at the beginning and at the end of each experiment in order to remove the possible alkali ions located on the catalyst surface and hence to define a reference catalyst state (un-promoted state). It can be observed that under both reaction atmospheres a strong catalyst deactivation took place from the first polarization which was attributed to the carbon deposition. However, it can be observed that the catalyst could be regenerated during the negative polarizations steps (under conditions of electrochemical pumping of ions) since the initial  $\text{H}_2$  production rates were restored in the last positive polarization at 2 V. As in the example of classical chemical promotion shown on Fig. 2, the alkali promotional effect can be explained in terms of modification of the chemisorption bond strength of the different reactants [39,61]. The back-spillover of electropositive ions onto the Pt active sites under negative polarization would lead to the decrease of the catalyst work function. Both the migration (back-spillover) of alkali promoter ions via EPOC and the concomitant modification of catalyst work function have been confirmed by means of different surface analysis techniques, as recently reviewed [26]. In this way, the chemisorption of electron acceptor molecules (i.e.,  $\text{H}_2\text{O}$  and, mainly,  $\text{O}_2$ ) would be strengthened under negative polarization favouring the removal of the carbon deposits. This hypothesis was confirmed by the successive temperature-programmed oxidation (TPO) experiments (Fig. 3b) carried out after exposing the catalyst to ATR conditions under two different polarization sequences: +2 V (i.e., un-promoted state), and +2 V followed by –1 V (i.e., after electrochemical supply of  $\text{Na}^+$  ions) [46]. In the latter case, a significant decrease in the carbon deposits was also found in good agreement with the results of chemical promotion shown on Fig. 2. These results demonstrate the interest of EPOC (Fig. 3) vs. classical promotion (Fig. 2). In both cases the same kind of alkali-derived promotional effect is observed but EPOC allows the catalyst activation (under promoter-free conditions) and regeneration (in the presence of alkali promoter) in a controllable and cyclic manner via the applied electric polarization.

In 1995, the group of prof. Vayenas already applied the EPOC concept to the methane steam reforming reaction [44]. In this case, a Ni-based catalyst film was supported on yttria-stabilized zirconia, i.e.,  $\text{ZrO}_2(\text{Y}_2\text{O}_3)$  (also denoted as YSZ), as solid electrolyte (i.e., as  $\text{O}^{2-}$ -conductor) as shown in Fig. 4a. Fig. 4b shows the dynamic response of reactor outlet stream composition to a potentiostatic transient from the open-circuit potential,  $V_{\text{WR}}^0$  (i.e., at current zero) which is the un-promoted state in this case, to  $V_{\text{WR}} = +1$  V. In this study, the positive polarization of the electrochemical catalyst led to the supply of  $\text{O}^{2-}$  ions from the solid electrolyte support to the catalyst film. This caused a decrease in the carbon deposition, leading to an increase in both methane conversion and CO production rate. The catalyst regeneration took place, in

contrast to the previously mentioned work using a  $\text{Na}^+$ -conductor electrolyte, upon anodic polarization because the carbon deposits were electrocatalytically oxidized (directly) by the  $\text{O}^{2-}$  ions. Nevertheless, the CO production rate was



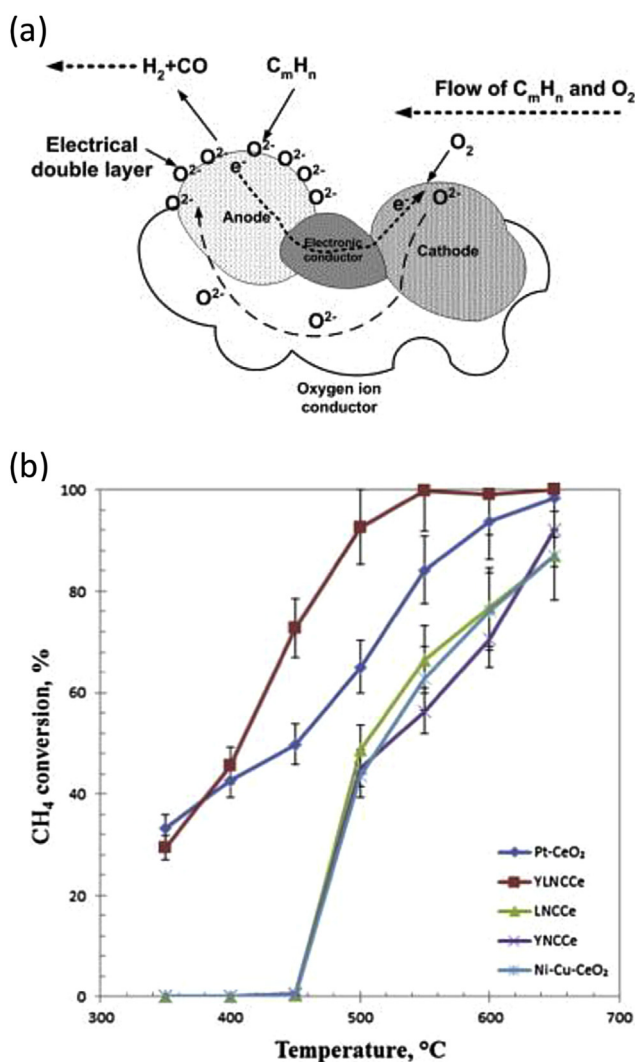
**Fig. 4** – (a) Schematic illustration of the oxide fuel cell reactor configuration. (b) Dynamic response of cell current and mole fractions of  $\text{H}_2\text{O}$ ,  $\text{CH}_4$  and  $\text{CO}$  in the cell reactor effluent to the application of an electric potential,  $V_{\text{WR}}$ , of +1 V at 800 °C. Catalyst: Ni/YSZ ( $\text{O}^{2-}$  conductor). Methane steam reforming conditions:  $\text{H}_2\text{O}/\text{CH}_4$  ratio of 0.6, 205  $\text{ccSTP min}^{-1}$ . Reprinted with permission from Ref. [44].

enhanced 57 times during this anodic polarization (vs. open-circuit conditions) and the rate increase was 15 times higher than that of the steady-state rate of  $\text{O}^{2-}$  ions supply (i.e., the faradaic maximum possible electrocatalytic CO oxidation rate), showing the promotional effect of the electrochemically supplied  $\text{O}^{2-}$  ions. One can find in literature other similar study of EPOC for the  $\text{H}_2$  production from methane reforming by depositing Pt nanoparticles onto a YSZ matrix [45].

In addition, it should be mentioned that a new way of electrochemical promotion, denoted as self-sustained electrochemical promotion (SSEP), has also been developed and applied in  $\text{H}_2$  production reactions via the partial oxidation of methane [62,63] and other heavy hydrocarbons [63–65]. In contrast to conventional EPOC studies, the SSEP concept does not require any external connections and electric polarization. This advantage also implies that it becomes more difficult to in-situ control the promoter coverage on the catalyst (as via external polarization). SSEP is based on the use of microscopic electrochemical galvanic cells composed by the following four components (schematized in Fig. 5a): microscopic selective anodic (Ni–Cu– $\text{CeO}_2$ ) and cathodic ( $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ ) phases, along with electronic conduction (Ni–Cu) and microscopic oxygen ion conduction (YSZ) phases between both electrodes. In this configuration, once the hydrocarbons and oxygen mixture is fed into the reactor,  $\text{O}^{2-}$  ions are produced at the perovskite-like cathode and migrate to the anode through the oxygen ion conductor material due to the different electrochemical potentials between both electrodes. The  $\text{O}^{2-}$  ions participate in the hydrocarbon oxidation reaction at the anode and the electrons derived from the reaction are driven to the cathode through the electronic conductor. For instance, Fig. 5b shows the  $\text{CH}_4$  conversion (via partial oxidation) obtained at different reaction temperatures with the self-sustained electrochemically promoted catalyst (denoted as YLNCCe). The results obtained were compared with those obtained with a similar catalyst lacking the cathode (YNGCe), a catalyst lacking the  $\text{O}^{2-}$  ion conductor (LNCGe) and two commercial catalysts (Pt– $\text{CeO}_2$  and Ni–Cu– $\text{CeO}_2$ ) [62]. It was found that above 400 °C, the SSEP catalyst presented the highest  $\text{CH}_4$  conversion as well as the highest  $\text{H}_2$  selectivity [62]. Then, all the studies mentioned above clearly demonstrated the interest of using electronic promoters on methane reforming and partial oxidation catalysts regardless the way of introducing them: chemically (classical promotion) or electrochemically via an applied electric current or potential (electrochemical promotion) or without any external polarization (SSEP mechanism).

### Chemical and electrochemical promotion of $\text{CH}_3\text{OH}$ conversion reactions

As in the case of methane conversion reactions, different metal oxide supports and alkali and alkaline-earth dopants are commonly employed to enhance the performance of the catalysts employed in the alcohols reforming reactions, e.g. methanol [19,20,66] and ethanol steam reforming [28,67,68]. For instance, Kusche et al. investigated the promotional effect of potassium hydroxide [31] and potassium acetate [30] molten salts added to Pt/ $\text{Al}_2\text{O}_3$  catalysts for the steam

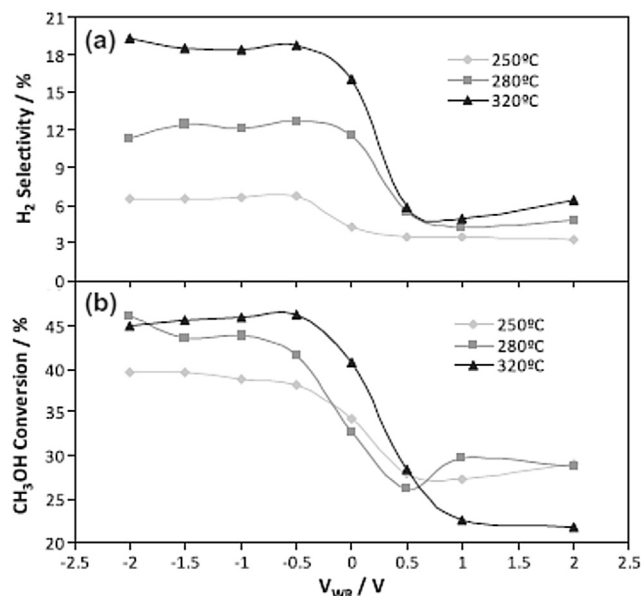


**Fig. 5 – (a) Schematic illustration of the concept of self-sustained electrochemical promotion (SSEP) catalysts for hydrocarbons partial oxidation. The catalysts consist of four coupled microscopic components: Ni–Cu–CeO<sub>2</sub> as selective anodic phase, La<sub>0.9</sub>Sr<sub>0.1</sub>MnO<sub>3</sub> as selective cathodic phase, YSZ as O<sup>2-</sup> ions conductor and Cu–Ni as electronic conductor. (b) CH<sub>4</sub> conversion variation with temperature over the SSEP catalyst (YLNNCe), similar catalysts lacking the cathode (YNCe) or the O<sup>2-</sup> ion conductor (LNCe) and Pt–CeO<sub>2</sub> and Ni–Cu–CeO<sub>2</sub> catalysts. Methane partial oxidation conditions: CH<sub>4</sub>/CO<sub>2</sub> ratio of 1.9, space velocity of 42000 h<sup>-1</sup>. Reprinted with permission from Refs. [65] and [62].**

reforming of methanol. It was reported that the Pt catalytic activity strongly depended on the KOH coverage, being the maximum methanol conversion obtained with an optimum KOH loading of 7.5 wt.% under given reaction conditions [31]. The detrimental effect of an excess of KOH was attributed to the mass transfer barrier introduced into the system by the progressive filling of the catalyst pores [31]. Regarding the promotional effect of certain potassium salts loadings, the authors attributed the enhancement in catalyst activity, at least in part, to the hygroscopic nature and basicity of these

salts, which allowed increasing water availability at the catalytic active sites and promoting the water-gas shift reaction step [30,31]. Furthermore, it has been demonstrated by spectroscopic studies that alkali doping weakens the C–H bond of methoxy and formate intermediate species in the methanol reforming reaction [30,33].

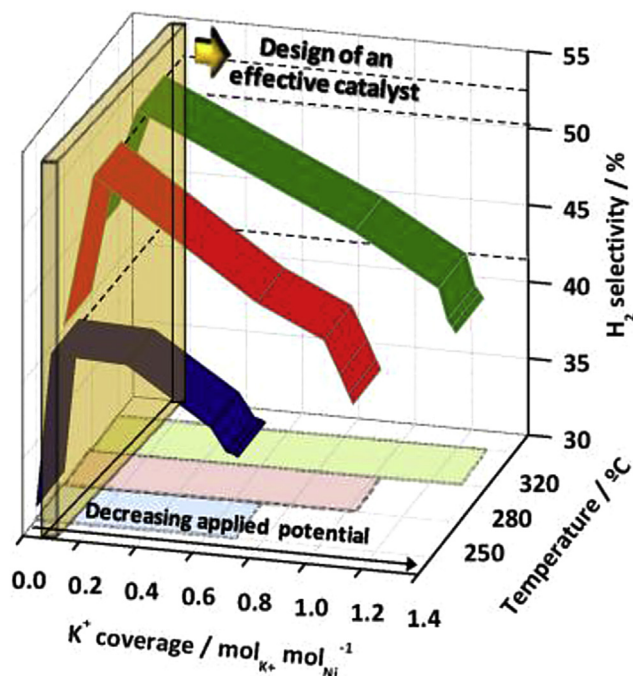
In 1989, S. Neophytides and C.G. Vayenas applied, for the first time, the electrochemical promotion to the methanol dehydrogenation reactions to produce H<sub>2</sub>, H<sub>2</sub>CO and CO by using a Pt/YSZ solid electrolyte cell [48]. In this study, a promotional effect was found upon decreasing the applied potential (i.e., upon removing O<sup>2-</sup> ions from the Pt catalyst surface). This was explained on the basis of the decrease of catalyst work function which would favour the chemisorption of electron acceptor molecules. Hence, the methanol dehydrogenation mechanism would be favoured due to the electron acceptor character of the methoxy group (CH<sub>3</sub>O) and the successive intermediate species (CH<sub>x</sub>O, x = 0–2) versus the intramolecularly bonded H [48] which is in good agreement with the previous discussion derived from classical chemical promotion studies [30,33]. More recently, our group have carried out several studies related to the electrochemical promotion of methanol conversion reactions for H<sub>2</sub> production by using alkaline conductors. In the first study the catalytic activity of a Pt catalyst film was enhanced by the in-situ electrochemical pumping of K<sup>+</sup> ions from a K-βAl<sub>2</sub>O<sub>3</sub> solid electrolyte (i.e., K<sup>+</sup>-conductor) in the methanol steam reforming reaction [49]. The EPOC concept was also applied in further studies under methanol decomposition [47], steam reforming [47], and partial oxidation [50–53] reaction conditions. In order to explore the different opportunities provided by this phenomenon and its possible practical utility in this kind of catalytic processes, several thin films prepared by physical vapour deposition of different metals such as Pt [50], Au [52], Cu [53] or Ni [47,51] were used. As an example of these studies, Fig. 6 shows the influence of the electrochemical promotion under methanol partial oxidation conditions on the activity and H<sub>2</sub> selectivity of a Pt catalyst film [50]. In this study, the decrease in the applied potential and, hence, the electrochemical supply of K<sup>+</sup> promoter ions to the Pt catalyst led to a clear increase in the catalytic activity in the studied temperature range. This can be attributed to the alkali-derived promotional effect on the methanol dehydrogenation mechanism, as previously mentioned, but also to the strengthening of the oxygen chemisorption upon decreasing the catalyst work function since the methanol partial oxidation reaction rate typically exhibits a positive order with respect to oxygen partial pressure for certain (low) O<sub>2</sub>-to-CH<sub>3</sub>OH ratios [69,70]. However, the most interesting feature from this figure is the fact that an increase in the potassium coverage improved not only the catalytic activity but also the selectivity toward the methanol partial oxidation instead of the total oxidation mechanism leading to an increase of the H<sub>2</sub> selectivity by a factor of four. This study shows that the electrochemical promotion, in contrast to classical chemical promotion, allows to in-situ enhance the catalytic activity and selectivity of a catalyst used in the hydrogen production from methanol, by means of the controlled pumping of alkali promoter ions. This operational advantage of the EPOC phenomenon was also pointed out with a catalyst composed of gold nanoparticles



**Fig. 6** – Effect of the applied potential ( $V_{WR}$ ) on the steady-state variation of (a) H<sub>2</sub> selectivity and (d) CH<sub>3</sub>OH conversion at different temperatures. Catalyst: Pt/K-βAl<sub>2</sub>O<sub>3</sub> (K<sup>+</sup> ions conductor). Methanol partial oxidation conditions: CH<sub>3</sub>OH/O<sub>2</sub> composition of 7.2%/4.6%, 6 Ndm<sup>3</sup> h<sup>-1</sup>. Reprinted with permission from Ref. [50].

[52], which were successfully electrochemically activated by K<sup>+</sup> ions. In this case hydrogen production rate was multiplied by up to 9 under optimum promotional conditions, but methyl formate was selectively obtained and H<sub>2</sub> selectivity remained still low after K<sup>+</sup>-induced enhancement.

One can find in literature other related studies of EPOC for the H<sub>2</sub> production from methanol using non noble metals. For instance, a Cu catalyst film prepared on a K-βAl<sub>2</sub>O<sub>3</sub> solid electrolyte by the physical vapour oblique angle deposition technique (PV-OAD), also called glancing angle deposition (GLAD), was electrochemically promoted for the methanol partial oxidation [53]. This catalyst was formed by Cu nanocolumns which provided higher porosity and surface area than the catalysts commonly employed in EPOC studies deposited, for instance, by calcination of an organometallic paste or impregnation of a precursor solution [40]. It should be noted that most of the EPOC studies in literature are generally focused on the use of catalyst films based on pure precious metals of low dispersion (<5%). This feature, along with the typically low surface area provided by the EPOC catalysts in three-electrodes configuration, makes it difficult for these catalysts to compete with conventional supported ones. In this sense, the development of catalyst films such as this Cu nanocolumnar film aims to overcome these obstacles. The obtained enhancement of Cu catalytic activity was even higher than that obtained with Pt-based catalyst films under similar reaction conditions [53]. The possible applications of the EPOC phenomenon were also evaluated with Ni-based catalyst films for methanol decomposition, steam reforming and partial oxidation reactions [47,51]. Fig. 7 shows the influence of the K<sup>+</sup> coverage on the H<sub>2</sub> selectivity under methanol



**Fig. 7** – Effect of K<sup>+</sup> coverage on H<sub>2</sub> selectivity at different temperatures. Catalyst: Ni-C/K-βAl<sub>2</sub>O<sub>3</sub> (K<sup>+</sup> ions conductor). Methanol partial oxidation conditions: CH<sub>3</sub>OH/O<sub>2</sub> composition of 4.4%/0.33%, 6 Ndm<sup>3</sup> h<sup>-1</sup>. Reprinted with permission from Ref. [51].

partial oxidation conditions using a dispersed Ni catalyst [51]. It can be clearly observed that there is an optimum concentration of promoter ions on the Ni catalyst which maximizes the H<sub>2</sub> selectivity at each reaction temperature. For example, at 250 °C one could obtain a selectivity increase of 135% by means of the in-situ electrochemical supply of K<sup>+</sup> ions to reach a promoter loading of only c.a. 10%, which is of the same order of magnitude as the optimum promoter loading values reported in classical promotion studies [30,31]. Moreover, depending on the K<sup>+</sup> coverage on the Ni catalyst surface and on the reaction atmosphere, different promotional effects were observed, apart from those related to the enhancement of the Ni catalytic activity and the modification of the catalytic selectivity, such as the attenuation of catalyst deactivation by carbon deposition or the in-situ alkali-induced nickel partial oxidation [47,51]. Furthermore, against other H<sub>2</sub> production technologies based on purely electrocatalytic systems, e.g. direct methanol electro-oxidation [8,9], the EPOC studies reviewed herein show a negligible electric energy consumption since the electric current applied in all these studies is of the order of only few microamperes.

Besides the aforementioned studies related to the electrochemical promotion of methanol conversion processes, a recent contribution of alkaline electrochemical catalysts must be highlighted, which consists on the simultaneous H<sub>2</sub> production and storage and its subsequent release under fixed mild operation conditions by only varying the applied electric current or potential [71]. This milestone was achieved with a nanocolumnar Ni catalyst film that was electrochemically promoted by K<sup>+</sup> ions under methanol steam reforming

conditions leading to a hydrogen storage capacity of 19 wt.% with respect to Ni. It is noteworthy the interest of this kind of electrocatalytic configurations for catalyst activation in methanol conversion processes but also for the in-situ separation and storage of the produced hydrogen which is one of the main hot topics in the hydrogen technology field nowadays [72,73].

### Chemical and electrochemical promotion of other catalytic reactions for H<sub>2</sub> production

Other important catalytic reaction for H<sub>2</sub> production and purification is the water-gas shift reaction (WGS), which is usually included in hydrocarbons and alcohols reforming processes in order to increase the overall hydrogen production yield and suppress the CO concentration in the outlet stream since this compound can severely poison the anode of the fuel cells particularly at low-temperature operation [74]. There is an extensive literature related to the chemical promotion of supported catalysts for the water-gas shift reaction [32–36,75]. Similarly to the methanol steam reforming promotion, in the water-gas shift reaction the alkali promotional effect is attributed to the hygroscopic nature of the alkaline salts, which increases the water availability to the catalytic active sites [32,75] and to the alkali-induced weakening of the formate C–H bond, being this cleavage considered the rate-limiting step in most cases [33–36]. Fig. 8 compares the variation of CO conversion and catalyst selectivity toward methane formation (which is a side product) with Ru/C catalysts prepared by the ethylene glycol reduced method (denoted as Ru/C-EG) and impregnated with different concentrations of K<sub>2</sub>CO<sub>3</sub> solution [75]. It is clearly observed that water-gas shift reaction rate is enhanced with the increase of the promoter coverage in the whole temperature range and that the methanation reaction is fully suppressed below 300 °C with the 10 wt.% K<sub>2</sub>CO<sub>3</sub> catalyst.

Similar effects have been found in previous EPOC studies carried out with Ni [55] and Pt [54] catalyst films by using K<sup>+</sup> and O<sup>2-</sup> ionic conductors supports, respectively. In both cases, an electrophilic EPOC behaviour was found, since the CO conversion was enhanced upon cathodic polarization, i.e., upon pumping/removal of K<sup>+</sup>/O<sup>2-</sup> ions to/from the catalyst film. In this way, the consequent strengthening of the chemisorption bond of electron acceptor molecules such as hydroxyl groups and the weakening of that of electron donors such as CO would cause the increase in the overall catalytic activity. An example of this effect can be observed in Fig. 9 for the case of a Pt/YSZ solid electrolyte cell [54]. The positive order of the water-gas shift reaction rate found with respect to steam partial pressure is in good agreement with the promotional effect based on water chemisorption strengthening (i.e., induced under cathodic polarization). The authors also attributed the enhancement of the water dissociation to the increase in surface concentration of oxygen ion vacancies near the Pt-YSZ-gas three-phase boundaries upon cathodic polarization [54]. On the other hand, the electrochemical promotion of the WGS reaction in a PEM fuel cell configuration with nafion membrane, Pt cathode and Pt or PtCu anodes [76,77] was also investigated in view of the practical

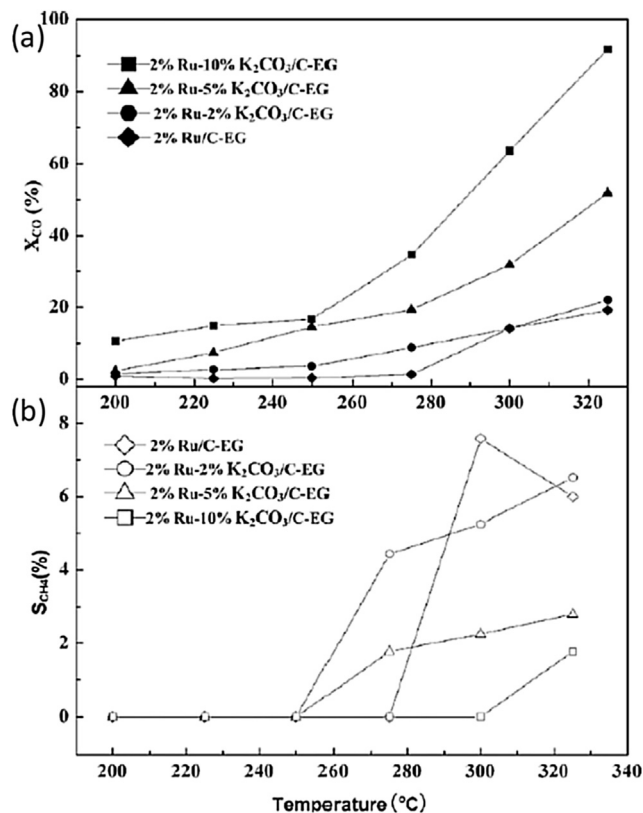


Fig. 8 – Effect of K<sub>2</sub>CO<sub>3</sub> loading on (a) CO conversion and CH<sub>4</sub> selectivity over a Ru/C catalyst at different temperatures. Water-gas shift conditions: CO/H<sub>2</sub>O composition of 1%/2%. Reprinted with permission from Ref. [75].

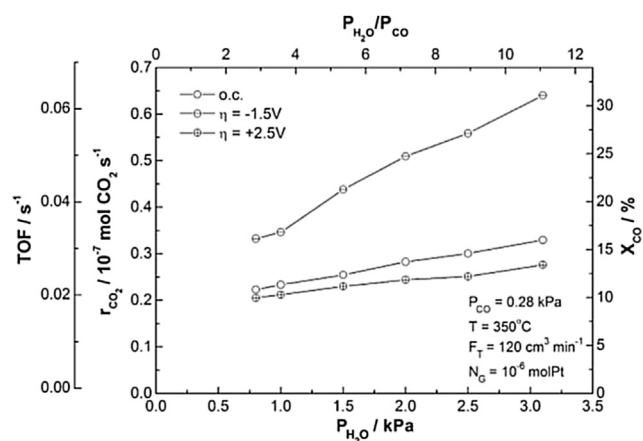
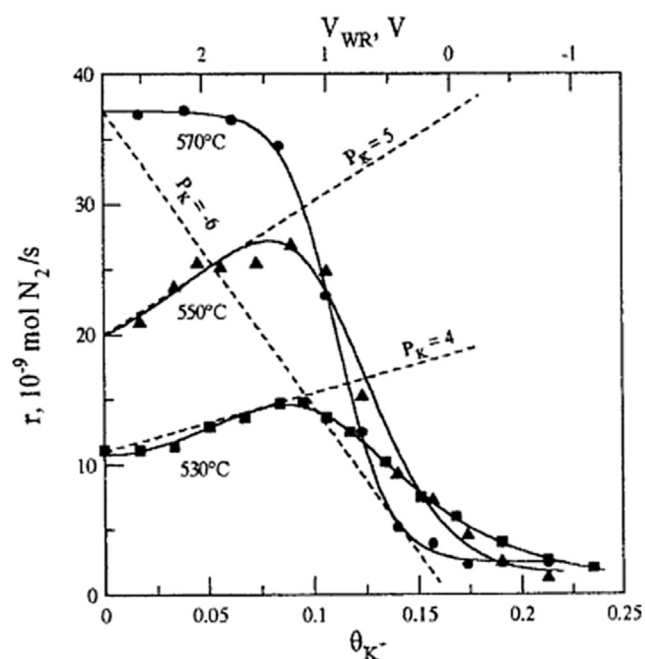


Fig. 9 – Effect of positive and negative polarization on CO<sub>2</sub> production rate and CO conversion at 350 °C. Catalyst: Pt/YSZ (O<sup>2-</sup> conductor). Water-gas shift conditions: CO partial pressure of 0.28 kPa and different H<sub>2</sub>O partial pressures, 120 cm<sup>3</sup> min<sup>-1</sup>. Reprinted with permission from Ref. [54].

application of the EPOC phenomenon for the in-situ treatment of CO-containing methanol reformat streams. However, the non-faradaic increase of CO consumption rate observed in fuel cell and oxygen bleeding operation modes was rather





**Fig. 10** – Effect of the applied potential ( $V_{WR}$ ) and the  $K^+$  coverage ( $\theta_{K^+}$ ) on  $NH_3$  decomposition reaction rate at different temperatures. Catalyst:  $Fe/K_2YZr(PO_4)_3$  ( $K^+$  conductor). Reprinted with permission from Ref. [56].

attributed to the  $O_2$  crossover through the membrane and the subsequent CO oxidation increase.

The phenomenon of the electrochemical promotion of catalysis has also been applied in other hydrogen production reactions, such as liquid-phase hydrazine decomposition in fuel cell configuration with Ni–Co anodes [78] and ammonia decomposition with Fe catalyst supported on  $K_2YZr(PO_4)_3$  (i.e.,  $K^+$ -conductor) [56]. In fact, this latter case is an example of a typical industrial alkali-promoted catalytic process [79,80]. Fig. 10 shows the variation of the ammonia decomposition reaction rate by using the  $Fe/K_2YZr(PO_4)_3$  electrochemical catalyst with the decrease of the applied potential ( $V_{WR}$ ) and the corresponding increase of the potassium coverage ( $\theta_{K^+}$ ) on the catalyst surface [56]. It can be observed that at temperatures below 550 °C the electrochemical supply of low amounts of potassium ions caused a 50% enhancement of the ammonia decomposition rate. The K-promotional effect can be attributed to the strengthening of nitrogen (i.e., electron acceptor) and the weakening of ammonia and hydrogen (i.e., electron donors). In particular, an optimum  $K^+$  coverage of c.a. 0.1 was found to maximize the ammonia conversion under the studied reaction conditions [56]. In this case the main advantage of the EPOC phenomenon against the classical promotion of ammonia decomposition is, again, the in-situ control of the promoter coverage and, thus, of the catalytic reaction rate.

## Conclusions and prospects

This paper collects several examples found in literature related to the chemical promotion and electrochemical promotion (EPOC) of different catalytic hydrogen production

reactions. Strong similarities can be observed between both kinds of promotion techniques. In all the cases, the nature and magnitude of the promotional effect depends on the nature and concentration of the electronic promoter, the reactants, the characteristics of the catalyst employed and the reaction conditions. However, chemical and electrochemical promotions are very different from the operational point of view. In the former, the amount of promoter is fixed from the catalyst preparation step; in the latter, the promoters are ions which are electrochemically supplied to the catalyst from a solid electrolyte support in the course of the catalytic reaction. Hence, the EPOC phenomenon is a useful tool for the in-situ optimization of the catalytic performance under changing reaction conditions, for instance, to maximize the catalytic selectivity toward a particular reaction product or to in-situ regenerate a catalyst deactivated by carbon deposition. This opens new possibilities of improving catalytic processes for the  $H_2$  production and new ways of operating catalytic systems by, for example, inducing catalytic activation and regeneration cycles. Hence, although the performance of the state-of-the-art EPOC catalysts, in terms of catalytic conversion, is still far from that of commercial catalysts, the electrochemical promotion provides a number of possibilities for in-situ action and a control over catalytic processes that, otherwise, would require the modification of the initial catalyst formulation or the operation conditions. Moreover, in contrast to conventional  $H_2$  production technologies based on direct water or alcohol electrocatalytic oxidation, in the case of EPOC the applied current is of the order of few microamperes, thus requiring negligible electric energy consumption for its operation.

Regarding the future, beyond expanding the study of the EPOC phenomenon to  $H_2$  production reactions with other hydrogen sources as raw materials, different metal catalysts or ion conductors, increasing efforts must be done for scaling-up reactors suitable for EPOC application such as tubular or monolithic catalyst configurations, where higher catalytic active surface areas will be provided while keeping the three-electrodes cell configuration. More competitive catalyst films configurations and catalyst preparation techniques should be also developed leading to systems based on non-noble metals with higher metal particle dispersions, i.e., more similar to commercial catalysts. It would also be interesting to focus on other new different applications of EPOC in hydrogen field. For instance, the possible activation, separation and storage of the  $H_2$  produced would open new opportunities that may contribute to the development of the technology for hydrogen production. The reversible and in-situ controllable nature of the electrochemical promotion could be further exploited by developing electrocatalytic systems where different catalytic processes may simultaneously take place and be enhanced on catalyst-electrodes deposited on both sides of the solid electrolyte. This way, coupled processes such as  $H_2$  production/catalyst regeneration or  $H_2$  storage/release could be cyclically operated by only switching the applied electric polarization. Moreover, the ease of operation, versatility and in-situ performance of the electrochemically promoted catalysts make them an ideal tool to optimize the promoter dose to be applied in these catalytic processes and in any other, with a view to

designing the most efficient catalytic formulations for the given application.

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## REFERENCES

- [1] Wails D. World hydrogen energy conference 2016: recent advances in a range of topics related to hydrogen and fuel cells. *Johns Matthey Technol Rev* 2017;61:29–31. <http://dx.doi.org/10.1595/205651317x693750>.
- [2] Dutta S. A review on production, storage of hydrogen and its utilization as an energy resource. *J Industrial Eng Chem* 2014;20:1148–56. <http://dx.doi.org/10.1016/j.jiec.2013.07.037>.
- [3] Cipriani G, Di Dio V, Genduso F, La Cascia D, Liga R, Miceli R, et al. Perspective on hydrogen energy carrier and its automotive applications. *Int J Hydrogen Energy* 2014;39:8482–94. <http://dx.doi.org/10.1016/j.ijhydene.2014.03.174>.
- [4] Dodds PE, Staffell I, Hawkes AD, Li F, Grünewald P, McDowall W, et al. Hydrogen and fuel cell technologies for heating: a review. *Int J Hydrogen Energy* 2015;40:2065–83. <http://dx.doi.org/10.1016/j.ijhydene.2014.11.059>.
- [5] Ursúa A, Gandía LM, Sanchis P. Hydrogen production from water electrolysis: current status and future trends. *Proc IEEE* 2012;100:410–26. <http://dx.doi.org/10.1109/jproc.2011.2156750>.
- [6] Carmo M, Fritz DL, Mergel J, Stolten D. A comprehensive review on PEM water electrolysis. *Int J Hydrogen Energy* 2013;38:4901–34. <http://dx.doi.org/10.1016/j.ijhydene.2013.01.151>.
- [7] Galán-Mascarós JR. Water oxidation at electrodes modified with earth-abundant transition-metal catalysts. *ChemElectroChem* 2014;2:37–50.
- [8] Lamy C, Guenot B, Cretin M, Pourcelly G. Kinetics analysis of the electrocatalytic oxidation of methanol inside a DMFC working as a PEM electrolysis cell (PEMEC) to generate clean hydrogen. *Electrochimica Acta* 2015;177:352–8. <http://dx.doi.org/10.1016/j.electacta.2015.02.069>.
- [9] Fathirad F, Mostafavi A, Afzali D. Bimetallic Pd–Mo nanoalloys supported on Vulcan XC-72R carbon as anode catalysts for direct alcohol fuel cell. *Int J Hydrogen Energy* 2017;42(5):3215–21.
- [10] González-Cobos J, Baranton S, Coutanceau C. Development of bismuth-modified PtPd nanocatalysts for the electrochemical reforming of polyols into hydrogen and value-added chemicals. *ChemElectroChem* 2016;3:1694–704. <http://dx.doi.org/10.1002/celec.201600147>.
- [11] Caravaca A, Sapountzi FM, De Lucas-Consuegra A, Molina-Mora C, Dorado F, Valverde JL. Electrochemical reforming of ethanol-water solutions for pure H<sub>2</sub> production in a PEM electrolysis cell. *Int J Hydrogen Energy* 2012;37:9504–13. <http://dx.doi.org/10.1016/j.ijhydene.2012.03.062>.
- [12] Hossain MA, Jewaratnam J, Ganesan P. Prospect of hydrogen production from oil palm biomass by thermochemical process – a review. *Int J Hydrogen Energy* 2016;41:16637–55. <http://dx.doi.org/10.1016/j.ijhydene.2016.07.104>.
- [13] Navarro RM, Sánchez-Sánchez MC, Alvarez-Galvan MC, Valle FD, Fierro JLG. Hydrogen production from renewable sources: biomass and photocatalytic opportunities. *Energy Environ Sci* 2009;2:35–54. <http://dx.doi.org/10.1039/b808138g>.
- [14] Walter MG, Warren EL, McKone JR, Boettcher SW, Mi Q, Santori EA, et al. Solar water splitting cells. *Chem Rev* 2010;110:6446–73. <http://dx.doi.org/10.1021/cr1002326>.
- [15] Angeli SD, Monteleone G, Giaconia A, Lemonidou AA. State-of-the-art catalysts for CH<sub>4</sub> steam reforming at low temperature. *Int J Hydrogen Energy* 2014;39:1979–97. <http://dx.doi.org/10.1016/j.ijhydene.2013.12.001>.
- [16] Navarro RM, Peña MA, Fierro JLG. Hydrogen production reactions from carbon feedstocks: fossil fuels and biomass. *Chem Rev* 2007;107:3952–91. <http://dx.doi.org/10.1021/cr0501994>.
- [17] Said SAM, Waseeuddin M, Simakov DSA. A review on solar reforming systems. *Renew Sustain Energy Rev* 2016;59:149–59. <http://dx.doi.org/10.1016/j.rser.2015.12.072>.
- [18] Gradisher L, Dutcher B, Fan M. Catalytic hydrogen production from fossil fuels via the water gas shift reaction. *Appl Energy* 2015;139:335–49. <http://dx.doi.org/10.1016/j.apenergy.2014.10.080>.
- [19] Sá S, Silva H, Brandão L, Sousa JM, Mendes A. Catalysts for methanol steam reforming-A review. *Appl Catal B* 2010;99:43–57. <http://dx.doi.org/10.1016/j.apcatb.2010.06.015>.
- [20] Yong ST, Ooi CW, Chai SP, Wu XS. Review of methanol reforming-Cu-based catalysts, surface reaction mechanisms, and reaction schemes. *Int J Hydrogen Energy* 2013;38:9541–52.
- [21] Mross WD. Alkali doping in heterogeneous catalysis. *Catal Rev* 1983;25:591–637.
- [22] Farrauto RJ, Bartholomew CH. *Fundamentals of industrial catalytic processes*. London: Chapman & Hall; 1997.
- [23] Ni C, Pan L, Yuan Z, Cao L, Wang S. Study of methane autothermal reforming catalyst. *J Rare Earths* 2014;32:184–8. [http://dx.doi.org/10.1016/s1002-0721\(14\)60049-1](http://dx.doi.org/10.1016/s1002-0721(14)60049-1).
- [24] Borowiecki T, Denis A, Rawski M, Gołębiowski A, Stołecki K, Dmytryk J, et al. Studies of potassium-promoted nickel catalysts for methane steam reforming: effect of surface potassium location. *Appl Surf Sci* 2014;300:191–200. <http://dx.doi.org/10.1016/j.apsusc.2014.02.053>.
- [25] Juan-Juan J, Román-Martínez MC, Illán-Gómez MJ. Effect of potassium content in the activity of K-promoted Ni/Al<sub>2</sub>O<sub>3</sub> catalysts for the dry reforming of methane. *Appl Catal A General* 2006;301:9–15. <http://dx.doi.org/10.1016/j.apcata.2005.11.006>.
- [26] Nagaraja BM, Bulushev DA, Beloshapkin S, Chansai S, Ross JRH. Potassium-doped Ni-MgO-ZrO<sub>2</sub> catalysts for dry reforming of methane to synthesis gas. *Top Catal* 2013;56:1686–94. <http://dx.doi.org/10.1007/s11244-013-0102-6>.
- [27] Barroso-Quiroga MM, Castro-Luna AE. Catalytic activity and effect of modifiers on Ni-based catalysts for the dry reforming of methane. *Int J Hydrogen Energy* 2010;35:6052–6. <http://dx.doi.org/10.1016/j.ijhydene.2009.12.073>.
- [28] Bshish A, Yaakob Z, Narayanan B, Ramakrishnan R, Ebshish A. Steam-reforming of ethanol for hydrogen production. *Chem Pap* 2011;65:251–66. <http://dx.doi.org/10.2478/s11696-010-0100-0>.
- [29] Denis A, Grzegorzczak W, Gac W, Machocki A. Steam reforming of ethanol over Ni/support catalysts for generation of hydrogen for fuel cell applications. *Catal Today* 2008;137:453–9. <http://dx.doi.org/10.1016/j.cattod.2008.03.006>.
- [30] Kusche M, Enzenberger F, Bajus S, Niedermeyer H, Bösmann A, Kaftan A, et al. Enhanced activity and selectivity in catalytic methanol steam reforming by basic alkali metal

- salt coatings. *Angew Chem - Int Ed* 2013;52:5028–32. <http://dx.doi.org/10.1002/anie.201209758>.
- [31] Kusche M, Agel F, Ní Bhriain N, Kaftan A, Laurin M, Libuda J, et al. Methanol steam reforming promoted by molten salt-modified platinum on alumina catalysts. *ChemSusChem* 2014;7:2516–26. <http://dx.doi.org/10.1002/cssc.201402357>.
- [32] Kusche M, Bustillo K, Agel F, Wasserscheid P. Highly effective Pt-based water-gas shift catalysts by surface modification with alkali hydroxide salts. *ChemCatChem* 2015;7:766–75. <http://dx.doi.org/10.1002/cctc.201402808>.
- [33] Evin HN, Jacobs G, Ruiz-Martinez J, Graham UM, Dozier A, Thomas G, et al. Low temperature water-gas shift/methanol steam reforming: alkali doping to facilitate the scission of formate and methoxy C-H bonds over Pt/ceria catalyst. *Catal Lett* 2008;122:9–19. <http://dx.doi.org/10.1007/s10562-007-9352-x>.
- [34] Evin HN, Jacobs G, Ruiz-Martinez J, Thomas GA, Davis BH. Low temperature water-gas shift: alkali doping to facilitate formate C-H bond cleaving over Pt/ceria catalysts—an optimization problem. *Catal Lett* 2008;120:166–78. <http://dx.doi.org/10.1007/s10562-007-9297-0>.
- [35] Gao P, Graham UM, Shafer WD, Linganis LZ, Jacobs G, Davis BH. Nanostructure and kinetic isotope effect of alkali-doped Pt/silica catalysts for water-gas shift and steam-assisted formic acid decomposition. *Catal Today* 2016;272:42–8. <http://dx.doi.org/10.1016/j.cattod.2015.07.007>.
- [36] Pigos JM, Brooks CJ, Jacobs G, Davis BH. Low temperature water-gas shift: the effect of alkali doping on the C-H bond of formate over Pt/ZrO<sub>2</sub> catalysts. *Appl Catal A* 2007;328:14–26. <http://dx.doi.org/10.1016/j.apcata.2007.04.001>.
- [37] Vayenas CG, Bebelis S, Pliangos C, Brosda S, Tsiplakides D. *Electrochemical activation of catalysis: promotion, electrochemical promotion and metal-support interactions*. New York: Kluwer Academic Publishers/Plenum Press; 2001.
- [38] de Lucas-Consuegra A. New trends of alkali promotion in heterogeneous catalysis: electrochemical promotion with alkaline ionic conductors. *Catal Surv Asia* 2015;19:25–37.
- [39] González-Cobos J, de Lucas-Consuegra A. A review of surface analysis techniques for the investigation of the phenomenon of electrochemical promotion of catalysis with alkaline ionic conductors. *Catalysts* 2016;6. <http://dx.doi.org/10.3390/catal6010015>.
- [40] Vernoux P, Lizarraga L, Tsampas MN, Sapountzi FM, De Lucas-Consuegra A, Valverde JL, et al. Ionically conducting ceramics as active catalyst supports. *Chem Rev* 2013;113:8192–260.
- [41] Konsolakis M, Palermo A, Tikhov M, Lambert RM, Yentekakis IV. Electrochemical vs. conventional promotion: a new tool to design effective, highly dispersed conventional catalysts. *Ionics* 1998;4:148–56.
- [42] Yentekakis IV, Lambert RM, Tikhov MS, Konsolakis M, Kioussis V. Promotion by sodium in emission control catalysis: a kinetic and spectroscopic study of the Pd-catalyzed reduction of NO by propene. *J Catal* 1998;176:82–92.
- [43] Tsiplakides D, Balomenou S. Electrochemical promoted catalysis: towards practical utilization. *Chem Industry Chem Eng Q* 2008;14:97–105.
- [44] Yentekakis IV, Jiang Y, Neophytides S, Bebelis S, Vayenas CG. Catalysis, electrocatalysis and electrochemical promotion of the steam reforming of methane over Ni film and Ni-YSZ cermet anodes. *Ionics* 1995;1:491–8.
- [45] Caravaca A, De Lucas-Consuegra A, Molina-Mora C, Valverde JL, Dorado F. Enhanced H<sub>2</sub> formation by electrochemical promotion in a single chamber steam electrolysis cell. *Appl Catal B Environ* 2011;106:54–62. <http://dx.doi.org/10.1016/j.apcatb.2011.05.004>.
- [46] de Lucas-Consuegra A, Caravaca A, Martínez PJ, Endrino JL, Dorado F, Valverde JL. Development of a new electrochemical catalyst with an electrochemically assisted regeneration ability for H<sub>2</sub> production at low temperatures. *J Catal* 2010;274:251–8.
- [47] González-Cobos J, López-Pedrajas D, Ruiz-López E, Valverde JL, De Lucas-Consuegra A. Applications of the electrochemical promotion of catalysis in methanol conversion processes. *Top Catal* 2015. <http://dx.doi.org/10.1007/s11244-015-0493-7>.
- [48] Neophytides S, Vayenas CG. Non-faradaic electrochemical modification of catalytic activity. 2. The case of methanol dehydrogenation and decomposition on Ag. *J Catal* 1989;118:147–63. [http://dx.doi.org/10.1016/0021-9517\(89\)90307-2](http://dx.doi.org/10.1016/0021-9517(89)90307-2).
- [49] de Lucas-Consuegra A, González-Cobos J, Gacia-Rodríguez Y, Endrino JL, Valverde JL. Electrochemical activation of the catalytic methanol reforming reaction for H<sub>2</sub> production. *Electrochem Commun* 2012;19:55–8. <http://dx.doi.org/10.1016/j.elecom.2012.03.016>.
- [50] de Lucas-Consuegra A, González-Cobos J, García-Rodríguez Y, Mosquera A, Endrino JL, Valverde JL. Enhancing the catalytic activity and selectivity of the partial oxidation of methanol by electrochemical promotion. *J Catal* 2012;293:149–57.
- [51] González-Cobos J, Ruiz-López E, Valverde JL, de Lucas-Consuegra A. Electrochemical promotion of a dispersed Ni catalyst for H<sub>2</sub> production via partial oxidation of methanol. *Int J Hydrogen Energy* 2016;41(42):19418–29.
- [52] González-Cobos J, Horwat D, Ghanbaja J, Valverde JL, De Lucas-Consuegra A. Electrochemical activation of Au nanoparticles for the selective partial oxidation of methanol. *J Catal* 2014;317:293–302.
- [53] González-Cobos J, Rico VJ, González-Elipse AR, Valverde JL, de Lucas-Consuegra A. Electrochemical activation of an oblique angle deposited Cu catalyst film for H<sub>2</sub> production. *Cat Sci Tec* 2015;5:2203–14.
- [54] Souentie S, Lizarraga L, Kambolis A, Alves-Fortunato M, Valverde JL, Vernoux P. Electrochemical promotion of the water-gas shift reaction on Pt/YSZ. *J Catal* 2011;283:124–32. <http://dx.doi.org/10.1016/j.jcat.2011.07.009>.
- [55] de Lucas-Consuegra A, Caravaca A, González-Cobos J, Valverde JL, Dorado F. Electrochemical activation of a non noble metal catalyst for the water-gas shift reaction. *Catal Commun* 2011;15:6–9.
- [56] Pitselis GE, Petrolekas PD, Vayenas CG. Electrochemical promotion of ammonia decomposition over Fe catalyst films interfaced with K<sup>+</sup> & H<sup>+</sup> conductors. *Ionics* 1997;3:110–6.
- [57] Sepehri S, Rezaei M, Garbarino G, Busca G. Preparation and characterization of mesoporous nanocrystalline La-, Ce-, Zr-, Sr-containing Ni-Al<sub>2</sub>O<sub>3</sub> methane autothermal reforming catalysts. *Int J Hydrogen Energy* 2016;41:8855–62. <http://dx.doi.org/10.1016/j.ijhydene.2016.03.139>.
- [58] Graf PO, Mojet BL, Lefferts L. The effect of potassium addition to Pt supported on YSZ on steam reforming of mixtures of methane and ethane. *Appl Catal A General* 2009;362:88–94. <http://dx.doi.org/10.1016/j.apcata.2009.04.022>.
- [59] Graf PO, Mojet BL, Lefferts L. Influence of potassium on the competition between methane and ethane in steam reforming over Pt supported on yttrium-stabilized zirconia. *Appl Catal A General* 2008;346:90–5. <http://dx.doi.org/10.1016/j.apcata.2008.05.010>.
- [60] Ali S, Al-Marri MJ, Abdelmoneim AG, Kumar A, Khader MM. Catalytic evaluation of nickel nanoparticles in methane steam reforming. *Int J Hydrogen Energy* 2016;41:22876–85. <http://dx.doi.org/10.1016/j.ijhydene.2016.08.200>.

- [61] Vayenas CG, Brosda S. Electron donation-backdonation and the rules of catalytic promotion. *Top Catal* 2014;57:1287–301.
- [62] Zhou X, Huang H, Liu H. Study of partial oxidation reforming of methane to syngas over self-sustained electrochemical promotion catalyst. *Int J Hydrogen Energy* 2013;38:6391–6. <http://dx.doi.org/10.1016/j.ijhydene.2013.03.047>.
- [63] Huang H, Wang Z, Zhou X, Liu H, Wei Y, Pramuanjaroenkij A, et al. Development and study of self-sustained electrochemical promotion catalysts for hydrocarbon reforming. 2 ed ECS Trans 2013:243–54. <http://dx.doi.org/10.1149/05802.0243ecst>.
- [64] Huang H, Wang Z, Liu H, Sun H, Wei Y, Zhou X. A kinetic model for analyzing partial oxidation reforming of heavy hydrocarbon over a novel self-sustained electrochemical promotion catalyst. *Int J Hydrogen Energy* 2012;37:15125–34. <http://dx.doi.org/10.1016/j.ijhydene.2012.07.128>.
- [65] Wang Z, Huang H, Liu H, Zhou X. Self-sustained electrochemical promotion catalysts for partial oxidation reforming of heavy hydrocarbons. *Int J Hydrogen Energy* 2012;37:17928–35. <http://dx.doi.org/10.1016/j.ijhydene.2012.09.072>.
- [66] Palo DR, Dagle RA, Holladay JD. Methanol steam reforming for hydrogen production. *Chem Rev* 2007;107:3992–4021. <http://dx.doi.org/10.1021/cr050198b>.
- [67] Contreras JL, Salmones J, Colín-Luna JA, Nuño L, Quintana B, Córdova I, et al. Catalysts for H<sub>2</sub> production using the ethanol steam reforming (a review). *Int J Hydrogen Energy* 2014;39:18835–53. <http://dx.doi.org/10.1016/j.ijhydene.2014.08.072>.
- [68] Dan M, Mihet M, Tasnadi-Asztalos Z, Imre-Lucaci A, Katona G, Lazar MD. Hydrogen production by ethanol steam reforming on nickel catalysts: effect of support modification by CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub>. *Fuel* 2015;147:260–8. <http://dx.doi.org/10.1016/j.fuel.2015.01.050>.
- [69] Ubago-Pérez R, Carrasco-Marín F, Moreno-Castilla C. Methanol partial oxidation on carbon-supported Pt and Pd catalysts. *Catal Today* 2007;123:158–63. <http://dx.doi.org/10.1016/j.cattod.2007.02.014>.
- [70] Espinosa LA, Lago RM, Peña MA, Fierro JLG. Mechanistic aspects of hydrogen production by partial oxidation of methanol over Cu/ZnO catalysts. *Top Catal* 2003;22:245–51.
- [71] González-Cobos J, Rico VJ, González-Elípe AR, Valverde JL, de Lucas-Consuegra A. Electrocatalytic system for the simultaneous hydrogen production and storage from methanol. *ACS Catal* 2016;6:1942–51. <http://dx.doi.org/10.1021/acscatal.5b02844>.
- [72] Dalebrook AF, Gan W, Grasmann M, Moret S, Laurenczy G. Hydrogen storage: beyond conventional methods. *Chem Commun* 2013;49:8735–51. <http://dx.doi.org/10.1039/c3cc43836h>.
- [73] Liu W, Webb CJ, Gray EM. Review of hydrogen storage in AB<sub>3</sub> alloys targeting stationary fuel cell applications. *Int J Hydrogen Energy* 2016;41:3485–507. <http://dx.doi.org/10.1016/j.ijhydene.2015.12.054>.
- [74] Cheng X, Shi Z, Glass N, Zhang L, Zhang J, Song D, et al. A review of PEM hydrogen fuel cell contamination: impacts, mechanisms, and mitigation. *J Power Sources* 2007;165:739–56. <http://dx.doi.org/10.1016/j.jpowsour.2006.12.012>.
- [75] Liu B, Huang T, Zhang Z, Wang Z, Zhang Y, Li J. The effect of the alkali additive on the highly active Ru/C catalyst for water gas shift reaction. *Catal Sci Technol* 2014;4:1286–92. <http://dx.doi.org/10.1039/c3cy00721a>.
- [76] Sapountzi FM, Tsampas MN, Vayenas CG. Methanol reformate treatment in a PEM fuel cell-reactor. *Catal Today* 2007;127:295–303.
- [77] Sapountzi F, Tsampas MN, Vayenas CG. Electrocatalysis and electrochemical promotion of CO oxidation in PEM fuel cells: the role of oxygen crossover. *Top Catal* 2007;44:461–8. <http://dx.doi.org/10.1007/s11244-006-0138-y>.
- [78] Sanabria-Chinchilla J, Asazawa K, Sakamoto T, Yamada K, Tanaka H, Strasser P. Noble metal-free hydrazine fuel cell catalysts: EPOC effect in competing chemical and electrochemical reaction pathways. *J Am Chem Soc* 2011;133:5425–31. <http://dx.doi.org/10.1021/ja111160r>.
- [79] Jedynak A, Kowalczyk Z, Szmigiel D, Raróg W, Zieliński J. Ammonia decomposition over the carbon-based iron catalyst promoted with potassium. *Appl Catal A General* 2002;237:223–6. [http://dx.doi.org/10.1016/s0926-860x\(02\)00330-7](http://dx.doi.org/10.1016/s0926-860x(02)00330-7).
- [80] Raróg W, Kowalczyk Z, Sentek J, Skladanowski D, Szmigiel D, Zieliński J. Decomposition of ammonia over potassium promoted ruthenium catalyst supported on carbon. *Appl Catal A General* 2001;208:213–6. [http://dx.doi.org/10.1016/s0926-860x\(00\)00721-3](http://dx.doi.org/10.1016/s0926-860x(00)00721-3).