

# **Electrochemical promotion of a dispersed Ni catalyst for H<sub>2</sub> production via partial oxidation of methanol**

**J. González-Cobos<sup>a,1</sup>, E. Ruiz-López<sup>a</sup>, J.L. Valverde<sup>a</sup>, A. de Lucas-Consuegra<sup>a,\*</sup>**

<sup>a</sup>Department of Chemical Engineering, School of Chemical Sciences and Technology,  
University of Castilla-La Mancha, Ave. Camilo José Cela 12, 13005 Ciudad Real, Spain

<sup>1</sup>Present address (J.G.-C). Institute of Chemical Research of Catalonia (ICIQ), Ave.  
Paisos Catalans 16, E-43007 Tarragona, Spain

\*Corresponding author. Tel.: +34-926295300; Fax: +34-926295437; E-mail address:

[Antonio.Lconsuegra@uclm.es](mailto:Antonio.Lconsuegra@uclm.es)

## **Abstract**

This study reports the electrochemical promotion (EPOC) of Ni particles dispersed in a diamond-like carbon (DLC) matrix. A Ni-DLC (Ni/C molar ratio of 0.1) catalyst film was prepared on a K- $\square$ Al<sub>2</sub>O<sub>3</sub> (K<sup>+</sup>-conductor) solid electrolyte by cathodic arc deposition (CAD). This physical vapour deposition (PVD) technique allows to decrease the metal loading used in the solid electrolyte cell and to electrochemically activate dispersed Ni particles in the methanol partial oxidation (POM) reaction by in-situ controlling the coverage of K<sup>+</sup> ions electrochemically transferred to the catalyst surface. As compared with a pure Ni layer prepared by the same technique, the Ni-DLC catalyst film shows a higher specific activity and an improved oxidation resistance under EPOC working reaction conditions. The possibility of electrochemically activate (with a negligible energy consumption) dispersed particles of a non-noble metal catalyst (closely related to commercially catalyst formulations) is of great interest for a further commercialization step of the EPOC phenomena in H<sub>2</sub> production reactions and in other catalytic systems.

**Keywords:** Electrochemical promotion; Dispersed catalyst; H<sub>2</sub> production; Partial oxidation; Alkali promotion; Ni-DLC catalyst

## 1. Introduction

The catalytic production of hydrogen from liquid carriers, e.g. methanol, is increasingly acquiring more importance given the facilities of these raw materials concerning their transport, storage and handling, among other advantages [1]. One can find in literature a large variety of catalysts (e.g. Pt, Pd, Cu, Ni,...) and supports (e.g. Al<sub>2</sub>O<sub>3</sub>, ZnO, SiO<sub>2</sub>,...) for H<sub>2</sub> production via steam reforming, partial oxidation and autothermal reforming of methanol [2-4]. Then, the development of novel catalytic configurations for this kind of processes is of great technological importance for the safe and efficient future utilization of hydrogen as a clean energy fuel. In this work we propose a relatively new approach based on the coupling of catalysis and electrochemistry through the concept of Electrochemical Promotion of Catalysis (EPOC). This phenomenon, discovered by Stoukides and Vayenas in 1981 [5], implies the controllable supply of ions (promoters), via an applied electric current or potential, from the catalyst support (which is a solid electrolyte material) to the catalyst surface (which is typically in form of a catalyst film). In fact, the origin of EPOC is essentially the same as that of classical promotion in heterogeneous catalysis by using electronic promoters. It is based on the ability of promoters ions to modify the chemisorption properties of the catalyst and hence to significantly alter the chemisorptive bond strength of reactants and intermediates [6, 7]. However, in the case of EPOC, the addition of the promoters is performed in-situ, i.e., in the course of the catalytic reaction, and hence, the amount of promoter can be easily modified (and controlled) by the external imposition of an applied electric potential [7-9]. In this way, it is possible to optimize the promoter coverage on the catalyst surface at varying reaction conditions. Furthermore, the EPOC phenomenon is not only aimed to enhance the catalytic activity and selectivity, but also may affect the reversible oxidation state of the catalyst [10-12] and can also be used to

prevent poisoning effects [11] and even to regenerate the catalyst from carbon deposition under working conditions [13].

For the last years, the EPOC phenomenon has been applied to enhance the catalytic properties of certain materials for the hydrogen production from methanol by using either yttria-stabilized zirconia (YSZ,  $O^{2-}$  conductor) [14-16] or  $K\text{-}\beta\text{-Al}_2\text{O}_3$  ( $K^+$  conductor) [11, 17] as solid electrolytes. However, most of these previous works were focused on the use of catalyst films based on pure precious metals of high metal loadings (up to 3 mg metal  $\text{cm}^{-2}$ ). This implies high-cost of the electrocatalytic configurations which makes it difficult to compete with conventional supported catalysts. Then, it is clear that in view of a possible practical application of EPOC, novel films based on metal catalysts of more competitive cost (non noble metals) and with higher metal particles dispersions should be investigated.

Herein, we propose for the first time in literature the electrochemical activation of a composite catalyst film based on Ni particles dispersed in a carbonaceous matrix (diamond-like carbon, DLC) which is an amorphous material with characteristics intermediate between those of graphite and diamond. DLC was selected as Ni-dispersing material due to its advantageous properties (e.g., high strength, thermal conductivity, low cost and chemical inertness in a wide range of reaction conditions) [18] and to the rich literature existing on films based on particles of Ni [19-23] and other metals (e.g., Pt [17, 24], Au [24], Ag [19], Ti [19, 25], Mo [20], Fe [20], Sn [20]) dispersed in DLC as catalyst support. Hence, in all these studies, the use of the DLC matrix allowed depositing stable metal nanoparticles while the internal stress of the DLC was decreased and its electrical conductivity was improved. In the present work, a Ni-DLC catalyst film has been deposited on a  $K\text{-}\beta\text{-Al}_2\text{O}_3$  solid electrolyte by cathodic arc deposition (CAD), which is a kind of physical vapour deposition (PVD) technique,

and the resultant electrochemical catalyst has been tested in the partial oxidation of methanol (POM). The effect of the electrochemical supply of  $K^+$  ions from the electroactive catalyst support to the Ni-DLC catalyst film has been investigated and evaluated in terms of EPOC promotional parameters under different reaction conditions. The stability of the Ni particles dispersed in the DLC under reaction conditions has also been checked. It has been demonstrated that the Ni-DLC catalyst film presents a higher specific activity than a pure Ni catalyst film prepared by the same method [11] and that these Ni particles can be reversibly electrochemically activated for the POM reaction, which shows the interest of the developed catalytic system.

## **2. Experimental**

### *2.1. Electrochemical catalyst preparation and characterization*

The electrochemical catalyst consisted of a continuous Ni-DLC thin film (geometric area of  $2.84 \text{ cm}^2$ ) deposited on a 19-mm-diameter, 1-mm-thick  $K-\square Al_2O_3$  (Ionotec) disc. In first place, Au counter (C) and reference (R) electrodes were deposited on one side of the electrolyte by applying thin coatings of gold paste (Gwent Electronic Materials C1991025D2), followed by calcination at  $800 \text{ }^\circ\text{C}$  for 2 h (heating ramp of  $5 \text{ }^\circ\text{C}/\text{min}$ ). Au was chosen as the auxiliary electrode material because of its inertness for the studied reaction conditions (checked via blank experiments). Then, the active Ni-DLC catalyst film, which also behaves as the working electrode (W), was deposited on the other side of the electrolyte by the filter cathodic arc deposition technique [26]. The deposition procedure was described in detail elsewhere [17] and it mainly consisted in the production of carbon and nickel plasmas from two cathodes contained in a mini-gun source designed to operate in pulsed mode. During the deposition, 25000 pulses (500 V, duty cycle of 10 %) were used and the  $K-\square Al_2O_3$  substrate holder was kept under rotating conditions (2 rpm). The resultant film presented a thickness of 240 nm, a Ni/C

atomic composition of 10.1 %/89.9 % and a metal loading of only  $0.006 \text{ mg}_{\text{Ni}} \text{ cm}^{-2}$ . For comparison purposes, a pure dense Ni film with a thickness of 150 nm and a metal loading of  $0.13 \text{ mg}_{\text{Ni}} \text{ cm}^{-2}$  was also prepared on a  $\text{K}-\square\text{Al}_2\text{O}_3$  solid electrolyte by using the same technique (filter cathodic arc). The obtained Ni-DLC surface was electrically nonconductive from its preparation, with an in-plane electrical resistance value of around  $50000 \text{ } \Omega \text{ cm}^{-1}$ . This surface electrical resistance was continuously measured (under open circuit conditions) by connecting two gold electric contacts on the Ni-DLC catalyst/working electrode to a digital multimeter. Hence, prior to the catalytic activity measurements, a temperature-programmed treatment similar to that described in a previous work [17] was carried out, by recording the variation of the in-plane electrical resistance of the catalyst surface vs. temperature. The catalyst film was subjected to a 25 %  $\text{H}_2$  stream (total flow of  $3.6 \text{ Ndm}^3 \text{ h}^{-1}$ , Ar balance) while it was heated to  $350 \text{ }^\circ\text{C}$  (ramp of  $3.5 \text{ }^\circ\text{C min}^{-1}$ ). This catalyst pre-treatment allowed decreasing the electrical resistance to a value of around  $600 \text{ } \Omega \text{ cm}^{-1}$ , which showed to be low enough to enable the electrochemical promotion of the Ni particles, as will be observed below. This modification of the electrical resistance was likely due to the partial graphitization of the DLC matrix with increasing temperature, as discussed in detail in previous works with metal-DLC composites [17, 27]. Moreover, in the previous work with a Pt-DLC composite film [17], an exhaustive characterization study was carried out both before and after the same temperature-programmed experiment than that carried out herein, thus demonstrating the increase in the graphitization degree of the DLC matrix with temperature increase and the stability of the metal nanoparticles. The three electrodes (working, counter and reference) were connected to an Autolab PGSTAT320-N potentiostat-galvanostat (Metrohm Autolab), and the electric potentials ( $V_{\text{WR}}$ ) were

applied according to the procedure generally used in conventional three-electrodes electrochemical cells [28].

The Ni-DLC catalyst film was firstly characterized via scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) analysis using a Quanta 250 scanning electron microscope with an EDX Apollo X detector (AMETEK) in order to check the catalyst surface composition and the Ni particles stability after the electrochemical promotion experiments. The catalyst film was also characterized by X-Ray Diffraction (XRD) analysis, using a Philips PW-1710 instrument with Cu K $\alpha$  radiation ( $\lambda = 1.5404$  Å), after exposure to methanol partial oxidation (POM) conditions ( $\text{CH}_3\text{OH}/\text{O}_2 = 4.4$  %/0.33 %, 320 °C) and different applied potentials. To this end, the following steps were carried out before each XRD analysis to keep the Ni unpromoted/promoted states as unaltered as possible: 1) Every time the Ni catalyst film was introduced into the reactor, a temperature-programmed reduction (TPR) was firstly performed under a 25 %  $\text{H}_2$  stream (Ar balance) from room temperature to 350 °C (ramp of 5 °C  $\text{min}^{-1}$ ) in order to ensure the Ni fully reduced state. 2) The catalyst was exposed for 1 hour to POM reaction conditions and to a given applied potential. 3) The reactor temperature was decreased to 100 °C by keeping constant the rest of reaction conditions. 4) The catalyst was finally cooled down to room temperature under Ar atmosphere under open circuit conditions. Then it was transferred to the characterization equipment in an inert atmosphere ( $\text{N}_2$  atmosphere).

## *2.2. Catalytic activity measurements*

The catalytic activity measurements were carried out in an experimental setup used in previous works by using a single chamber solid electrolyte cell reactor configuration [11, 17]. The reaction gases (Praxair, Inc.) were certified standards (99.999 % purity) of air (source of oxygen),  $\text{H}_2$  (reducing agent) and Ar (carrier gas). The gas flow rates were

controlled by a set of calibrated mass flowmeters (Bronkhorst EL-FLOW). Methanol (Panreac, 99.8% purity) was introduced to the feed stream by sparging Ar through a thermostated saturator. All lines placed downstream from the saturator were heated above 100 °C to prevent condensation. The catalytic experiments were carried out at atmospheric pressure with an overall gas flow rate of 6 Ndm<sup>3</sup> h<sup>-1</sup>, a composition of CH<sub>3</sub>OH/O<sub>2</sub> = 4.4 %/0.33 % (Ar balance) and a temperature ranging from 250 to 320 °C. Reactant and product gases were on-line analyzed with a double-channel gas chromatograph (Bruker 450-GC) equipped with Hayesep and Q-Molsieve 13X consecutive columns and a CP-Wax 52 CB capilar column, along with thermal conductivity (TCD) and flame ionization (FID) detectors. All the products reaction rates have been normalized per total amount of deposited Ni (2.9 x 10<sup>-7</sup> mol<sub>Ni</sub> and 6.45 x 10<sup>-6</sup> mol<sub>Ni</sub> for Ni-DLC and Ni films, respectively), thus being expressed in units of mol s<sup>-1</sup> mol<sub>Ni</sub><sup>-1</sup>. **The error in the carbon atom balance did not exceed 5 % in any experiment, which indicated no consistent loss of material, no significant formation of other oxygenated species, coking of the catalyst or oxidation of the carbonaceous matrix under the studied reaction conditions.**

### **3. Results and discussion**

#### *3.1. Characterization of the Ni-DLC catalyst film*

Figure 1 shows the top view SEM image of the Ni-DLC catalyst film after all the electrochemical promotion experiments, along with the corresponding EDX spectrum. In these images Ni particles (in white) were found to be dispersed on the DLC surface (dark regions), as also observed in SEM micrographs reported in other studies where DLC showed to favour the growth of nickel nanospheres instead of metal layers or extended grains [21, 23]. Al, O and K pertaining to the underlying K-βAl<sub>2</sub>O<sub>3</sub> solid electrolyte were also detected by EDX analysis. **As can be observed on the SEM**



micrographs, a fairly dense Ni-DLC catalyst film with a low roughness was obtained, in contrast to other kinds of configurations like, for instance, DLC foam structures [29]. In this case, the catalyst morphology was based on Ni particles dispersed in the DLC matrix as also reported in previous studies [19-21], being the surface area of the resultant catalyst film a difficult measurable parameter. Although the resolution of these SEM images did not allow appreciating nickel particle sizes below 100 nm, the presence of these dispersed particles, even after the catalytic activity measurements at 320 °C, denotes the enhanced thermal stability and wear resistance of metal-DLC composites commonly shown in literature [30, 31]. Hence, the stabilization of the Ni particles by the DLC matrix under the studied reaction conditions is in good agreement with the high structure stability reported in literature for other metal-DLC composites [17, 32-34], annealed even at 800 °C [34]. Hence it is possible to avoid thermal sintering problems typically taking place in thin pure catalyst films prepared by physical vapour deposition techniques [35, 36].

Figure 2a shows the post-reaction XRD diffractogram of the Ni-DLC catalyst film obtained after exposure to POM reaction conditions and an applied potential ( $V_{WR}$ ) of -2 V for 1 hour, which led to the electrochemical supply of  $K^+$  promoter ions to the catalyst surface (electropromoted state), as will be discussed later. No diffraction lines associated with DLC or other surface compounds that may be formed under reaction conditions were detected. All the peaks relative to the K- $\beta$ - $Al_2O_3$  support (JCPDS, 02-0921) can be clearly identified (cf. Figure 2b). The three main diffraction peaks of metallic nickel, i.e., (111), (200) and (220) are indicated at  $2\theta = 44.5^\circ$ ,  $51.8^\circ$  and  $76.4^\circ$ , which would be associated with a face-centered cubic (FCC) crystalline structure (JCPDS, 87-0712). These peaks are overlapped with some alumina peaks and their signals are very low as compared to those of the latter, probably due to the very small

Ni-DLC film thickness and the low metal loading. From Figure 2.a, an average Ni particle size can also be calculated from the width of the main diffraction peak, Ni(111), by means of the Scherrer equation [37]:

$$d / \text{\AA} = \frac{K_W \lambda}{B \cos\theta} \quad (1)$$

where  $\lambda$  is the X-ray wavelength (in  $\text{\AA}$ ), B is the full width at half maximum (FWHM) of the diffraction peak (in radians) corrected for instrumental broadening,  $\theta$  is the Bragg angle and  $K_W$  is the half-width Scherrer constant which is 0.86 in this case, given the cubic crystalline structure [38]. In this way, an average Ni particle size of around 25 nm is estimated in this Ni-DLC film. This value is of the same order than those obtained in other studies using Ni-DLC composites prepared by physical vapour deposition methods [19-21]. For instance, Usman et al. calculated Ni particle sizes between 23 and 40 nm from the XRD spectra [21]. It should also be noted that the obtained value of Ni particle size is lower than that obtained in a pure Ni catalyst film prepared by a similar deposition procedure (cathodic arc deposition), i.e., 31-35 nm [11], and than those obtained in other studies with less dispersed Ni catalyst films prepared by conventional methods like decomposition of a Ni organometallic paste [39] or impregnation of a precursor solution [40], which led to particle sizes between 30 and 100 nm.

### *3.2. Electrochemical promotion of the Ni-DLC catalyst film*

The phenomenon of electrochemical promotion of catalysis (EPOC) has been studied on the Ni-DLC catalyst film deposited on the  $K^+$ -conductor material for the hydrogen production via methanol partial oxidation (POM), with a feed composition of  $CH_3OH/O_2 = 4.4\% / 0.33\%$  (Ar balance). Figure 3 shows the influence of the applied potential ( $V_{WR}$ ) on the Ni catalytic activity, on the obtained current and on the potassium coverage at 280 °C. The latter parameter was calculated via Faraday law as will be shown bellow. The obtained products were  $H_2$ , CO,  $H_2CO$ ,  $CO_2$  and  $H_2O$  (the

latter is not depicted). Hydrogen, carbon monoxide and formaldehyde can be formed via methanol decomposition reactions (equations 1 and 2) and, in the presence of oxygen, methanol partial oxidation (equations 3 and 4) and deep oxidation (equation 5) may take place, also producing CO<sub>2</sub> and H<sub>2</sub>O.



Hence, Figure 3a shows the dynamic response of the production rates of H<sub>2</sub>, CO, H<sub>2</sub>CO and CO<sub>2</sub> obtained under the application of different potentials between +2 and -2 V. Each potential was imposed for 1 hour in order to reach an steady-state reaction value. As in previous EPOC studies using alkaline solid electrolytes [8, 28], a reference positive potential ( $V_{\text{WR}} = 2$  V, established from preliminary cyclic voltammetry measurements) was applied at the beginning and at the end of the experiment for the removal from the catalyst of the alkali ions that may have previously migrated from the solid electrolyte (e.g., by thermal diffusion) [41, 42]. In this way, an unpromoted catalyst surface is defined as a reference state. Then, it can be observed that after a certain decrease of the applied potential (at  $V_{\text{WR}} = 0.5$  V), all the production rates increased and negative current (I) values were obtained (see Figure 3b). The current is related to the electrochemical transfer of K<sup>+</sup> ions (which mostly occurred at the beginning of each polarization) from the K-βAl<sub>2</sub>O<sub>3</sub> pellet to the Ni-DLC catalyst film through the Faraday Law (equation 6).

$$\text{Promoter supply} / \text{mol}_{\text{K}^+} = \int_0^t \frac{(-I)dt}{nF} \quad (7)$$

where  $n$  is the potassium ion charge (+1),  $F$  is the Faraday constant ( $96485 \text{ C mol}_e^{-1}$ ) and  $t$  is the polarization time. Then, one can calculate the accumulated potassium coverage from the integration of the current vs. time curve, by considering the total amount of Ni deposited ( $N$ ), through the following equation:

$$K^+ \text{ coverage} / \text{mol}_{K^+} \text{mol}_{Ni}^{-1} = \frac{\int_0^t \frac{(-I)dt}{nF}}{N} \quad (8)$$

The evolution of this parameter is depicted in Figure 3c. Hence, the observed modification of the Ni catalytic activity with the applied potential can be attributed to the electrochemical supply of the electropositive ions and the consequent decrease of the catalyst work function [43-45]. According to previous studies on EPOC [17, 46] and classical chemical promotion [47, 48], the back-spillover of alkali ions to the catalyst surface would favour the methanol decomposition and partial oxidation reactions, likely through a dissociative adsorption mechanism. For instance, after the application of  $V_{WR} = 0.5 \text{ V}$ , a potassium coverage of 0.11 was reached which largely increased the production rates. However, the further decrease of the applied potential below 0.5 V caused the decrease of the  $H_2$ , CO and  $H_2CO$  production rates. The presence of an optimum potassium coverage value (0.11, in this case) has been widely observed in literature [42, 44, 49, 50] and the subsequent poisoning effect can be mainly attributed to an excess of alkali-derived surface compounds, like potassium carbonates, that may be formed and partially block Ni active sites. On the other hand,  $CO_2$  was the only product which was increasingly produced by decreasing the applied potential, which is likely related to the enhancement of  $O_2$  chemisorption and the favouring of the methanol deep oxidation mechanism (as well as the total oxidation of the produced CO and formaldehyde). Therefore the Ni-DLC catalyst film was optimally promoted by the electrical polarization of 0.5 V, involving a negligible electric energy consumption, which was of the order  $10^{-3} \text{ J}$ .

It is also very important to note that, after the final application of  $V_{WR} = 2$  V for 1 hour, the potassium ions were transferred back to the solid electrolyte (i.e., the  $K^+$  coverage practically vanished, as can be observed in Figure 3c) and all the production rates were restored to their initial un-promoted values. This demonstrates the full reversibility of the electropromotional effect and the possibility of controlling the Ni-DLC catalytic activity by varying the applied potential, despite the low electrical conductivity of the composite film. In addition, the obtained catalytic data verified the catalyst film stability after long working times (almost 10 h). This reproducible behaviour at the final application of 2 V was observed in all the performed electrocatalytic experiments in the explored conditions range and additionally supported by the in-plane electrical resistance measurements which showed no apparent sintering or modification of catalyst morphology.

Figure 4 shows the influence of the reaction temperature and the applied potential (after 1 h of polarization) on the steady-state production rates under the same methanol partial oxidation conditions. As expected, the overall Ni-DLC catalytic activity and most of the production rates were favoured by increasing the temperature in the whole potential range. In the case of formaldehyde, an optimum temperature of 280 °C seemed to be found, probably due to its further oxidation to  $CO_2$  at higher reaction temperature [51, 52]. It should be noted that, in all cases, the methanol conversion values obtained were kept below 5 %, which can be attributed to the low Ni metal loading, the low catalyst-electrode geometric area and the reactor design with very likely some reactant bypass. Under the three studied temperatures, the maximum  $H_2$ , CO and  $H_2CO$  production rates were obtained under an optimum potential of  $V_{WR} = 0.5$  V and the application of successive lower potentials led to the above mentioned poisoning effect.

In order to quantify the magnitude of the electropromotional effect, two parameters are typically used in the EPOC studies with alkaline conductors: the reaction rate enhancement ratio ( $\rho$ ) and the promotion index ( $PI_{K^+}$ ), which are defined for each compound (i) by the following equations:

$$\rho_i = \frac{r_i}{r_{i,0}} \quad (9)$$

$$PI_{K^+,i} = \frac{\frac{\Delta r_i}{r_{i,0}}}{K^+ \text{ coverage}} \quad (10)$$

where  $r_i$  and  $r_{i,0}$  are the promoted ( $V_{WR} < 2$  V) and unpromoted ( $V_{WR} = 2$  V) production rates, respectively, and  $\Delta r_i = r_i - r_{i,0}$  is the  $K^+$ -induced modification of the production rate. Under given reaction conditions,  $\rho$  is the factor by which the production rate of one product is increased at certain applied potential with respect to its unpromoted value, while  $PI_{K^+}$  provides a measure of the catalytic activity enhancement normalized by the promoter concentration created on the catalyst surface.

Figure 5 shows the variation of the rate enhancement ratios obtained under each applied potential in the previous experiments. The corresponding promotion indexes are also indicated for the optimum applied potential ( $V_{WR} = 0.5$  V) in each case. It can be observed that the reaction rate enhancement ratios decreased as the temperature was increased, which can be attributed to the higher unpromoted production rates ( $r_0$ ) obtained. As an exception,  $CO_2$  rate enhancement ratios increased with temperature and the maximum EPOC parameters values were obtained at a lower applied potential in this case, probably due to the favouring of the methanol total oxidation under these operation conditions. Among the different obtained products, hydrogen showed the highest  $\rho$  values at 280 and 250 °C, being its production rate increased in 2.1 and 2.4 times, respectively, under optimum promotional conditions. On the other hand, the  $PI_{K^+}$  values generally decreased from 250 to 320 °C, which is likely due to the increasing

solid electrolyte ionic conductivity with temperature and the consequent increase of  $K^+$  coverage reached at fixed potential (0.05, 0.11 and 0.16 at 250, 280 and 320 °C, respectively, at  $V_{WR} = 0.5$  V). This feature would also explain the sharpening of the poisoning effect taking place at the lowest potentials, which led to obtain production rate enhancement ratios far below unity at 320 °C.

In order to better evaluate the suitability of the electropromoted catalyst for the  $H_2$  catalytic production, Figure 6 shows the influence of the temperature and the  $K^+$  coverage on the  $H_2$  production selectivity, which has been calculated as follows:

$$H_2 \text{ Selectivity} / \% = \frac{F_{H_2,out}}{2x(F_{CH_3OH,in} - F_{CH_3OH,out})} \times 100 \quad (11)$$

where  $F_{H_2,out}$  is the obtained molar flow rate of hydrogen, and  $F_{CH_3OH,in}$  and  $F_{CH_3OH,out}$  are the methanol molar flow rate at the inlet and outlet of the reactor, respectively.

It can be clearly observed the positive effect of the temperature increase on the  $K^+$  coverage in the applied potential range due to the increase in the ionic conductivity of the solid electrolyte. It should be noted that potassium coverage even increased above 1 at 280 and 320 °C at the lowest applied potentials, which means that, under these reaction conditions, the number of  $K^+$  ions electrochemically transferred to the catalyst film was higher than the number of Ni sites. This may cause the partial blockage of active catalytic sites by the formation of potassium-derived surface compounds, as discussed above, and it can explain the decrease in the overall catalytic activity found at potentials below 0 V (see the sharp decrease of  $H_2$ , CO and  $H_2CO$  production rates and reaction rate enhancement ratios in figures 4 and 5, respectively). In addition, the  $H_2$  selectivity increased with the reaction temperature in the explored temperature range in good agreement with previous studies on partial oxidation of methanol with conventional catalysts [53, 54]. It is interesting to note that a maximum value of hydrogen selectivity was reached at each reaction temperature, due to the

electropromotional effect of an optimum  $K^+$  coverage in the range from 0 to 0.3 (marked by a shaded box inserted in the figure). Specifically,  $H_2$  selectivity increased up to around 41, 50 and 52 % at 250, 280 and 320 °C, respectively, under optimum electropromoted conditions. It should also be noted that, by comparing the results obtained at 320 °C under unpromoted conditions (i.e., 2 V) and those obtained at 280 °C under optimum promoted conditions (i.e., 0.5 V), which led to very similar overall catalytic activity (overall methanol conversion of around 3 % in both cases), the  $H_2$  selectivity obtained was 43 and 50 %, respectively. This denotes the interest of the EPOC phenomenon in activating a catalyst film for  $H_2$  production at lower temperature. As it was previously reported with a Pt-DLC catalyst film [17], the reaction rate of the different methanol oxidation products can be controlled by means of the potassium coverage. These results demonstrate that, in a certain range of potassium coverage, the electrochemical promotion allows enhancing not only the activity of the dispersed nickel catalyst but also its selectivity toward the methanol partial oxidation mechanism instead of the methanol deep oxidation reaction. Beyond, the EPOC phenomenon is postulated as a useful tool for the in-situ optimization of the catalytic performance and, hence, for the design of more effective catalysts formulations.

### *3.3. Comparison of the catalytic behaviour of the Ni-DLC and a pure Ni catalyst films*

The catalytic activity of the proposed Ni-DLC film was compared with that obtained with a pure Ni film used in a previous work [11] under both unpromoted and electropromoted conditions. Figure 7 shows the steady-state variation of the different production rates obtained with the two electrochemical catalysts under given POM reaction conditions ( $CH_3OH/O_2 = 4.4 \text{ \%}/0.33 \text{ \%}$ , 280 °C) and different applied potentials. Under unpromoted reaction conditions ( $V_{WR} = 2 \text{ V}$ ), all the (normalized) production rates obtained with the Ni-DLC catalyst film are higher than those obtained



with the pure metal catalyst. Considering that specific activities (normalized per overall Ni loading) of two Ni catalyst films are compared, the higher activity of the Ni-DLC catalyst can be attributed to its higher dispersion (higher fraction of accessible Ni sites). A catalyst dispersion value (D) of around 5 % can be calculated by means of the following equation [55]:

$$D / \% = \frac{6M_m}{\rho_m N_A \sigma d} \quad (12)$$

where  $M_m$  is the nickel atomic weight,  $\rho$  is the Ni density (in  $\text{g m}^{-3}$ ),  $N_A$  is the Avogadro number,  $d$  is an average Ni particle diameter (i.e., 250 Å) and  $\sigma$  is the metal atomic surface,  $5.38 \times 10^{-20} \text{ m}^2 \text{ atom}^{-1}$ , as obtained for the preferential plane, i.e., Ni(111). This dispersion value was higher than that previously obtained with pure Ni catalyst films where not all the Ni sites were accessible. A pure Ni catalyst prepared by cathodic arc deposition presented a dispersion of 3.6 % [11], and Ni catalysts prepared by conventional methods like impregnation of a precursor solution led to dispersion values around 1 % [40]. However, the most striking feature drawn from this comparison is the very different EPOC behaviour found on the two catalysts under cathodic polarization. With a pure Ni catalyst, when the applied potential was decreased to  $V_{\text{WR}} = 0.5 \text{ V}$ , the overall catalytic activity and the production rates of  $\text{H}_2$  and CO sharply dropped. This deactivation was attributed to the  $\text{K}^+$ -promoted strengthening of the metal-oxygen chemisorptive bond and the formation of oxidized Ni species on the catalyst surface. Other metals (e.g., Ru [10] or Rh [12]) supported on YSZ also showed to be oxidized/reduced upon cathodic/anodic polarization. Hence, the partially oxidized nickel catalyst was only slightly activated for  $\text{CO}_2$  and  $\text{H}_2\text{CO}$  production while it was inactive for  $\text{H}_2$  and CO production. In fact, nickel is widely used for the methanol decomposition and steam reforming reactions [56, 57], but it is not prone to the catalytic partial oxidation of methanol due to the formation of inactive nickel oxide [58, 59].

Instead, when the Ni-DLC film was polarized at  $V_{WR} = 0.5$  V, the production rate of  $H_2$  and the other compounds were enhanced likely due to the promotional effect of potassium ions on the methanol reaction mechanism. In order to confirm this observation, XRD analysis was carried out on the two catalyst films after exposure to POM reaction conditions under both unpromoted ( $V_{WR} = 2$  V) and electropromoted ( $V_{WR} < 2$  V) conditions. In the four diffractograms shown in Figure 8, the peaks related to the solid electrolyte and to the nickel can be observed. On the pure Ni catalyst film, other peaks associated with Ni oxides were found after negative polarization (Figure 8b), which were not detected after positive polarization (Figure 8a). This suggested that the electrochemical supply of  $K^+$  ions favoured the oxygen chemisorption and the consequent nickel partial oxidation, leading to the sharp decrease of the reaction rate observed in Figure 7. However, in the case of the DLC-dispersed Ni particles catalyst film, no nickel oxide peaks were found even after polarizing the sample at  $V_{WR} = -2$  V in the presence of oxygen (Figure 8d), which makes less noticeable the possible oxidation of this catalyst. In previous studies with conventional supported Ni catalysts an increase of the dispersion of the metal particles was associated with an increase of their reducibility [56, 60] and with a decrease of the nickel oxidation kinetics [61]. Ni-DLC composite also showed a high stability and tolerance upon  $O_2$  plasma etching, which was attributed to the high chemical reactivity between Ni and carbon [62]. Hence, the potassium-derived enhancement of the catalytic activity observed in Figure 7 for the Ni-DLC film under cathodic polarization can be tentatively attributed to an increase in the stability and oxidation resistance of the Ni particles embedded in this composite vs. the non-dispersed pure Ni film. The diamond-like carbon matrix would then play a key role as structural promoter for the Ni particles. **The incorporation of this carbonaceous material not only allowed decreasing the total amount of metal and**

increasing the particles dispersion, but also increased the stability of the Ni particles and hampered their partial oxidation under the studied reaction conditions. In this way, it was possible to activate dispersed Ni particles with alkali ions for H<sub>2</sub> production from methanol partial oxidation and the obtained results are encouraging in view of the practical application of the phenomenon of electrochemical promotion.

#### **4. Conclusions**

The following conclusions can be drawn from this study:

- A thin catalyst film composed of Ni particles dispersed in a diamond-like carbon (DLC) material was prepared by the cathodic arc deposition technique, employing a low metal loading and showing a good stability under the studied reaction conditions.
- The Ni-DLC catalyst film showed to be active for the hydrogen production from methanol partial oxidation and was successfully promoted by the electrochemical transfer of K<sup>+</sup> ions from a solid electrolyte. i.e., the Ni catalytic activity and H<sub>2</sub> production selectivity were in-situ improved in a controlled and reversible way by only varying the applied potential, with a negligible electric consumption.
- As compared to a pure dense Ni catalyst film, the Ni-DLC composite not only presented a higher specific catalytic activity, but also an enhanced chemical stability under electrochemical promotion conditions. Then, the proposed catalyst configuration may be of great interest for the further development of competitive catalyst films for H<sub>2</sub> production via electrochemical promotion.

#### **Acknowledgments**

The authors gratefully acknowledge the Spanish Ministry of Economy and Competiveness (Project CTQ2013-45030-R) for the financial support of this work.

## FIGURE CAPTIONS

**Figure 1.** SEM micrograph of the used Ni-DLC catalyst film (a, b) and its corresponding EDX elemental analysis (c).

**Figure 2.** XRD diffractogram of the used electrochemical catalyst after exposure to methanol partial oxidation conditions (320 °C CH<sub>3</sub>OH/O<sub>2</sub> = 4.4 %/0.33 %, Ar balance) and an applied potential ( $V_{WR}$ ) of -1 V for 1 h (a) along with the XRD-pattern of the K- $\beta$ Al<sub>2</sub>O<sub>3</sub> solid electrolyte (b).

**Figure 3.** Dynamic response of H<sub>2</sub>, CO, CO<sub>2</sub> and H<sub>2</sub>CO production rates (a), obtained electric current (I) (b) and potassium coverage (c) to step changes in the applied potential ( $V_{WR}$ ) under methanol partial oxidation conditions: 280 °C, CH<sub>3</sub>OH/O<sub>2</sub> = 4.4 %/0.33 %, Ar balance.

**Figure 4.** Steady-state H<sub>2</sub> (a), CO (b), CO<sub>2</sub> (c) and H<sub>2</sub>CO (d) production rates vs. the applied potential ( $V_{WR}$ ) under methanol partial oxidation conditions (CH<sub>3</sub>OH/O<sub>2</sub> = 4.4 %/0.33 %, Ar balance) at different reaction temperatures.

**Figure 5.** Steady-state H<sub>2</sub> (a), CO (b), CO<sub>2</sub> (c) and H<sub>2</sub>CO (d) production rate enhancement ratios ( $\rho$ ) vs. the applied potential ( $V_{WR}$ ) along with the corresponding maximum promotion indexes ( $PI_{K^+}$ ) obtained under the same methanol partial oxidation conditions as in Figure 4.

**Figure 6.** Influence of temperature and K<sup>+</sup> coverage on the hydrogen selectivity obtained under the same methanol partial oxidation conditions as in Figure 4. The shaded box inserted in the figure depicts the optimum electropromoted conditions resulting in the maximum H<sub>2</sub> production at given reaction conditions.

**Figure 7.** Steady-state H<sub>2</sub> (a), CO (b), CO<sub>2</sub> (c) and H<sub>2</sub>CO (d) production rates vs. the applied potential ( $V_{WR}$ ) obtained with the Ni-DLC and a pure Ni catalyst films under methanol partial oxidation conditions: 280 °C, CH<sub>3</sub>OH/O<sub>2</sub> = 4.4 %/0.33 %, Ar balance.

**Figure 8.** XRD diffractograms of the used Ni (a, b) and Ni-DLC catalyst films obtained after exposure for 1 h to unpromoted ( $V_{WR} = 2$  V) and electropromoted ( $V_{WR} < 2$  V) methanol partial oxidation conditions.

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