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Short Communication

# Electrochemical activation of a non noble metal catalyst for the water–gas shift reaction

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ABSTRACT

A novel electrochemical catalyst (Ni/K-$\beta Al_2O_3$/Au) has been prepared, characterized and tested under electrochemical promotion conditions for the water gas shift reaction. At 350 °C, under CO/$H_2O$: 1%/3% composition, negative potential applications in the single chamber cell, i.e., $K^+$ supplied ions to the active Ni catalyst film, caused a strong increase in the catalytic reaction rate for $H_2$ production (maximum rate enhancement ratio $\rho = 2.7$ at optimal potential conditions). The promotional phenomenon was found to be reversible due to the activation of $H_2O$ molecules chemisorption vs. CO with the consequent formation of active OH species. The achieved results show potential for the practical application of the phenomenon of electrochemical promotion of catalysis in the activation of base metal catalysts for this kind of processes.

## 1. Introduction

The production of pure hydrogen is essential for several processes; for instance, in ammonia production and power generation by hydrogen-based low temperature fuel cell technology. At present, hydrogen is generally produced by steam reforming and partial oxidation of methane or other carbonaceous feed stocks, which yield gas mixtures containing significant amounts of CO. The water gas shift (WGS) reaction is commonly applied to purify the obtained hydrogen:

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g) \quad (1)$$

$$\Delta H^\circ = -41.1 Kj/mol$$

Possible on-board reforming of fuels in connection with fuel cell-powered vehicles has created a renewed interest in WGS catalysts [1]. Recently, Ni-based catalysts have been recognized as an alternative catalyst [2–4] for the single-stage WGS reactor configuration. The use of Ni based catalysts facilitates the control of the heat of reaction and allows a higher catalytic conversion to be maintained with the isothermal conditions because of their high heat-conductivity. For instance, a recent investigation has demonstrated the better catalytic activity of Ni in comparison with Pt or Rh catalyst for the WGS reaction [5].

On the other hand, previous works have also demonstrated that Ni catalyst can be chemically promoted with potassium increasing its catalytic performance for the WGS process [6].

In the last years the coupling of the electrochemistry to catalysis through the phenomenon of electrochemical promotion (EPOC) has became an alternative approach to electrochemically supply and control a promoter concentration at the surface of a working metal catalyst [7–10]. This phenomenon, discovered by Stoukides and Vayenas in 1981 [11], also known as NEMCA effect (non-faradic electrochemical modification of catalyst activity), occurs when catalytic reactions take place on a metal film in contact with a solid electrolyte, where the latter acts as a source of electrochemically controlled promoter species [12–15]. Thus, until now, this phenomenon has been demonstrated in more than 80 catalytic systems with several important technological possibilities, particularly in industrial product selectivity and in exhaust gas treatment [16,17]. However, to the best of our knowledge, one can find in literature only some few works on the application of NEMCA effect to the WGS reaction [18,19]. In addition these works have used noble metal based electrochemical catalyst such as Pd deposited on a proton conducting support [18] or Pt deposited on YSZ [19]. One can also find in literature some other recent approaches made by the group of Prof. Vayenas [20–22] using PEM fuel cell configurations and other related studies, recently revised by Garagounis et al. [23], on the use of solid electrolyte cells on the WGS reaction.

The aim of this work is then to demonstrate for the first time the possibility of applying the phenomenon of electrochemical promotion in the activation of a base metal catalyst, with more competitive cost (such as Ni), for this kind of processes. Hence, a novel Ni/K-$\beta Al_2O_3$/Au

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electrochemical catalyst has been prepared, characterized and tested under electrochemical promotion conditions for the WGS reaction.

## 2. Experimental

The activity measurements were carried out in an experimental setup described in detail in a previous work by using a single chamber solid electrolyte cell reactor configuration [24]. In order to follow and check the reducibility and conductivity of the Ni catalyst-film, one additional electric contact was added to the catalyst-working electrode and connected to a digital multimeter. The catalytic experiments were carried out at atmospheric pressure with an overall gas flow rate of 6 L.h$^{-1}$ with the following composition: CO/$H_2O$ = 1%/3% at 350 °C. Reactant and product gasses were analyzed with a micro gas-chromatograph (Varian CP-4900).

The solid electrolyte cell consisted of a porous, continuous, thin Ni film (4 mg of Ni, geometric area of 2.01 cm$^2$) deposited on a side of a 19-mm-diameter, 1-mm-thick K-$\beta Al_2O_3$ (Ionotec) disc. The Au counter/reference (C/R) electrode was deposited on the other side of the electrolyte. This electrode was deposited by applying thin coatings of gold paste (Gwent Electronic Materials C1991025D2), followed by calcination at 800 °C for 2 h. Then, the active Ni catalyst film (W), which also behaves as a working electrode, was deposited by thermal decomposition of a $Ni(NO_3)_2$ solution, following previous works with Pt films [24]. Au was chosen as the auxiliary electrode material because of its inertness for WGS reaction (checked via blank experiments) which makes it an adequate pseudoreference electrode when using the single pellet design, as already discussed in a previous work [25].

Prior to the catalytic activity measurements, the catalyst film was reduced under a $H_2$ stream of 400 ppm ($N_2$ balanced) with an overall flow rate of 6 L.h$^{-1}$ under temperature programmed conditions (5 °C/min) from room temperature to 800 °C. The temperature programmed reduction process was in-situ monitored (TPR experiment) by recording the variation of the electrical resistance across the Ni catalyst-film along with the $H_2$ consumption rate (by fast analysis with the micro GC, one analysis per 1.5 min) vs. temperature. The TPR conditions (low heating ramp and low $H_2$ concentration) were selected to facilitate the monitoring of the reduction process of the Ni catalyst film due to the limited sensibility of the micro GC for this kind of experiment. After reduction, X-ray diffraction patterns of the catalyst-working electrode film were recorded on a Philips PW 1710 instrument using Ni-filtered Cu $K_\alpha$ radiation. The morphology of the catalyst film was also investigated via scanning electron microscopy (SEM), using a FEI Nova NANOSEM 230 instrument.

## 3. Results and discussion

Fig. 1 shows the results of the Temperature Programmed Reduction experiment (TPR) carried out in-situ in the single chamber solid electrolyte reactor. Fig. 1a shows the corresponding $H_2$ consumption rate vs. temperature under temperature programmed reduction conditions (5 °C/min) while Fig. 1b shows the variation of the electrical resistance of the Ni catalyst film. It can be observed that at the beginning of the TPR experiment, the deposited Ni based catalyst film showed a high value of electrical resistance ($64 \times 10^6$ Ω). It seems to indicate that the as-prepared catalyst film was on its oxidized form (NiO), typically obtained after the nitrate precursor decomposition method [26]. However, above 300 °C, the electrical resistance of the catalyst film decreased to almost a negligible value down to 1 Ω at 600 °C (zoom of Fig. 1b) probably due to the reduction of the NiO particles to Ni. A similar reduction temperature range has been found in a previous work [4] for the reduction of unsupported Ni bulk catalyst. This reduction can be further confirmed by the $H_2$ consumption peak shown in Fig. 1a which demonstrated that the beginning of the reduction took place around 300 °C. Finally it should be mentioned that after the TPR experiment, the Ni catalyst film was completely reduced as verified by XRD analysis shown in Fig. 2, which shows the XRD patterns of the catalyst film. The peaks at 2θ = 44.5, 51.8 and 76.4 were identified [2,3,6] as the typical diffraction peaks of Ni metal while the rest of peaks could be attributed to the K-$\beta Al_2O_3$ solid electrolyte support [8]. From the shape analysis of the main Ni diffraction peak at 2θ = 44º and the Scherrer's equation one can estimate an overall value of the Ni particle size (100 nm) and catalyst film dispersion of 0.84% in good agreement with previous catalyst films prepared by the impregnation method [8]. No peaks of NiO appeared for the reduced sample showing a total reduction of the initially oxidized Ni species. On the other hand, it is also interesting to note that due to the presence of $H_2$ in the water gas shift catalytic experiments, the reduction of the Ni catalyst film was preserved during the catalytic experiments. This assumption was verified by the

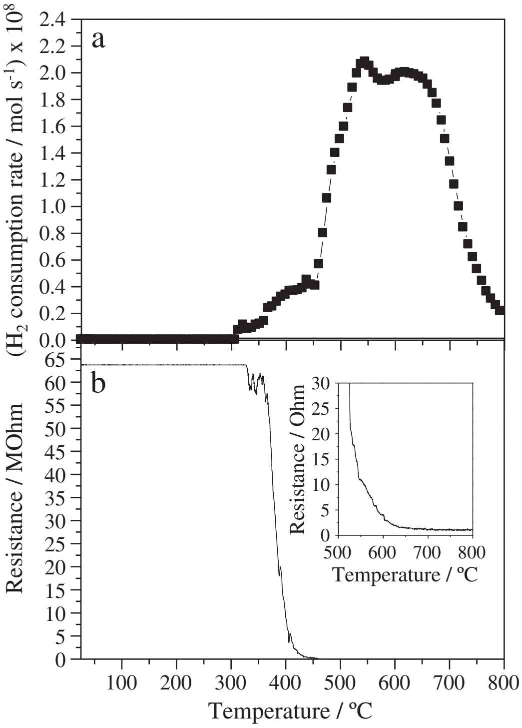

**Fig. 1.** $H_2$ consumption rate (a) and electrical resistance variation (b) of the Ni catalyst film during the temperature programmed reduction experiment (TPR). Heating rate of 5 °C/min under 400 ppm of $H_2$ stream ($N_2$ balanced).

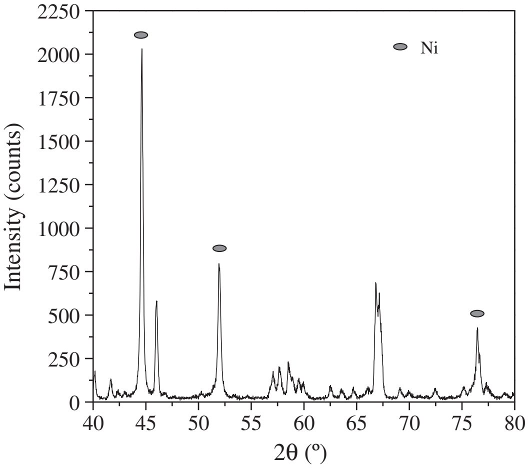

**Fig. 2.** XRD analysis of the Ni catalyst-working electrode film after reduction (TPR).