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Development of a new electrochemical catalyst with an electrochemically assisted regeneration ability for H_2 production at low temperatures

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ABSTRACT

A new electrochemical catalyst (Pt–Pt/YSZ/Na–βAl_2O_3) has been prepared and characterized for the H_2 production at low temperature from CH_4 with a high CO_2 selectivity. It has been tested under electrochemical promotion conditions under different reaction systems: steam reforming, partial oxidation and autothermal steam reforming. Among them, the latter system seems to be the most suitable one for the operation of the electrochemical catalyst in a cyclical way between positive and negative polarizations. Under positive polarization, the electrochemical catalyst produced a high amount of H_2. However, it was deactivated due to a strong increase in the CH_4-derived chemisorption species, which led to carbon deposition. Nevertheless, the subsequent application of negative polarization led to a strong increase in the coverage of O_2- and H_2O-derived species that caused the removal of the deposited carbon and, hence, the regeneration of the catalyst. The possibility of in situ electrochemical regeneration of a catalyst under fixed conditions could have a significant importance from both theoretical and technological points of view.

1. Introduction

Hydrogen has been attracting great interest as a future clean fuel for combustion engines and fuel cells [1]. Thus, efficient and compact production processes of hydrogen should be investigated for such application purposes. Nowadays, different technologies have been developed for H_2 production, which have been described in detail by means of excellent reviews [2–8]. Among them, methane steam reforming (SRM) is one of the most important and interesting techniques because of the abundance of natural gas (main source of methane) and its economic advantage versus other processes:

$$CH_4 + H_2O \rightarrow 3H_2 + CO, \quad \Delta H^0_{298} = 206\ \mathrm{kJ\ mol^{-1}} \quad (1)$$

The SRM process is typically carried out at high temperature (>750 °C) due to the high endothermic character of the reaction. Then, for further development of fuel cell systems with a reformer, it would be desirable to reduce the size and moderate the reaction conditions of the process.

In addition, the strict requirement of low CO amount in low-temperature fuel cells feeding stream implies further CO removal units. In this sense, the simultaneous water gas shift reaction (WGS, reaction 2) in the same reaction atmosphere by adding an excess of water could simplify the overall process, and hence the hydrogen production cost could be substantially reduced.

$$CO + H_2O \leftrightarrow CO_2 + H_2, \quad \Delta H^0_{298} = -41\ \mathrm{kJ\ mol^{-1}} \quad (2)$$

The carbon deposition is also a common limitation of SRM catalysts [9]. It leads to a progressive decrease in the number of catalytic actives sites with the consequent deactivation of the catalyst. Its possible regeneration would be the only way for the technical implementation of these systems. The use of excess of steam in the gas mixture or the addition of O_2 to the reaction atmosphere, through an autothermal steam reforming process (ATR), has been demonstrated to be useful techniques to partially solve this problem [10].

Thus, current intense research efforts are being placed to develop new catalyst configurations, which are able to overcome the above-mentioned limitations for on-board H_2 production from methane. In this work, we propose a novel approach to improve the performance of these processes by using an electro-active catalyst support (solid electrolyte) through the concept of electrochemical promotion [11]. This phenomenon, also known as NEMCA effect (non-Faradaic electrochemical modification of catalytic activity) was discovered by Stoukides and Vayenas in 1981 [12]. It is based on the control, by an applied potential, of the catalyst work function, due to electrochemical pumping of ions (promoters) from or to the solid electrolyte support [13–19]. At present, this phenomenon is considered as one of the latest

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advances in the field of heterogeneous catalysis and has been demonstrated in more than 80 catalytic systems with several important technological possibilities, particularly in industrial product selectivity and in exhaust gas treatment [20,21]. However, to the best of our knowledge, there is only one previous work on the application of the NEMCA effect to the SRM reaction [22]. In this earlier work, carried out by the group of Prof. Vayenas, the effect of electrochemical pumping of O^{2-} ions was investigated on the catalytic properties of a Ni catalyst film supported on YSZ (yttria-stabilized zirconia). However, the use of Ni/YSZ electrochemical catalyst produced high amount of CO (up to 90%) and only moderate modifications in the activity of the catalyst was observed under electrical polarization. The latter could be attributed to the high operation temperature of the system, above 800 °C, which probably led to a low stability of the promotional ions. One can find in literature other related studies on the conversion of methane through reforming, partial oxidation and autothermal reforming conditions [23–26] using solid electrolyte cells. These works, which have not explicitly used the terms NEMCA or electrochemical promotion, have followed an experimental procedure similar to the one reported here, but again under relatively high operation temperatures up to 900 °C, which led to an important CO production. Also, the high reaction temperatures used on these studies probably led to electrocatalytic processes instead of electrochemical promotional ones.

Then, the challenge of the present work is to develop a new electrochemical catalyst based on Pt that should fulfil the following requirements:

(i) Being active at low temperatures, compatible with the NEMCA effect (around 500 °C), for the SRM reaction.
(ii) Being active for the water gas shift reaction and therefore with high CO_2 selectivity in the overall process (SRM + WGS).
(iii) Being able to be electrochemically promoted under working reaction conditions in order to improve its catalytic performance, for instance, by regenerating the catalyst from carbon deposition.

The selection of Pt as the active catalyst film on the solid electrolyte cell was based on previous studies [27,28], which have demonstrated its better performance for CH_4 reforming process in comparison with other metals such as Rh, Ir and Ru. For instance, Pt supported on YSZ seems to be one of the most suitable and promising catalyst for SRM, showing high activity and stability for long operation times [29]. On the other hand, it is well known that alkalis promote the activation of water in SRM, which helps to remove hydrocarbon fragments from the surface [30]. Hence, a cationic solid electrolyte (Na–βAl_2O_3) was used as the electro-active support in the solid electrolyte cell with the aim to promote the regeneration of the catalyst.

2. Experimental

2.1. Catalytic activity measurements

The catalytic activity measurements were carried out in an experimental setup described in detail in a previous work [31]. The reaction gases (Praxair, Inc.) were certified standards of 4% CH_4/N_2, O_2/N_2 (21% purity) and N_2 (99.999% purity), which was used as the vector gas. The gas flow was controlled by a set of calibrated mass flowmeters (Brooks 5850 E and 5850 S) while water was introduced to the feed stream by means of a triple saturator in order to achieve liquid–vapour equilibrium. The content of water in the reaction mixture was controlled using the vapour pressure of H_2O at the temperature of the saturator (29 °C). All lines placed downstream from the saturator were heated above 100 °C to prevent condensation. The saturation of the feed stream by water at the working temperature was verified by a blank experiment where the amount of water trapped by a condenser was measured for certain time and compared with the theoretical value. The reactants were introduced into the reactor with the following concentrations: CH_4 (1%), H_2O (4%), O_2 (0–2000 ppm) balanced with N_2 with an overall gas flow rate of 6 L h^{-1}. Three different reaction compositions (shown in Table 1) were tested on this work, denoted as SRM (steam reforming of methane), ATR (autothermal steam reforming) and MPO (methane partial oxidation). All the catalytic experiments were carried out at 500 °C and atmospheric pressure. Reactant and product gases were analysed with a micro-gas chromatograph (Varian CP-4900) equipped with two columns (Molsieve and Poraplot Q column) and two thermal conductivity detectors (TCD). Before the analysis, the water was trapped by a condenser at -2 °C. Constant voltages across the cell were imposed using a potentiostat–galvanostat Voltalab 21 (Radiometer Analytical). All analysers' outputs, as well as the potentiostat–galvanostat outputs (current and potential), were continuously monitored and recorded.

2.2. Electrochemical catalyst preparation

The electrochemical catalyst consisted of a porous, continuous, thin Pt film (geometric area of 2.84 cm^2) deposited on a side of a 19-mm-diameter, 1-mm-thick Na–βAl_2O_3 disc (Ionotec). In first place, Au counter/reference 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, two different Pt films were prepared on the other side of the electrolyte according to two preparation methods. In the first sample (Pt/Na–βAl_2O_3, denoted henceforth as "P sample"), a thin coating of a commercial platinum paste (Metalor Code 6706) was applied on the electrolyte followed by calcination at 600 °C for 1 h. In the second sample (Pt–Pt/YSZ/Na–βAl_2O_3, denoted as "PPY sample"), the film was prepared by depositing a catalyst ink, self-prepared in our laboratory, on the solid electrolyte. The catalyst ink was prepared by mixing 40 mg of the commercial Pt paste with ethylene glycol to achieve a suitable sample viscosity, and 20 mg of a dispersed Pt/YSZ catalyst powder. This catalyst powder was prepared by a conventional impregnation procedure, where YSZ (yttria-stabilized zirconia) powder (Tosoh) was impregnated with a $H_6PtCl_6 \times 6H_2O$ precursor solution in a glass vessel under vacuum at 90 °C to yield 3% weight of Pt. After drying overnight at 120 °C, the resulting powder was calcined at 450 °C for 1 h. After the deposition of the ink over the solid electrolyte, it was finally annealed at 600 °C for 1 h. The electrodes (working and counter/reference) were connected to the potentiostat–galvanostat. The catalyst potential (V_{cell}) was applied according to the procedure generally used in conventional three-electrode electrochemical cells [13,15]. Before catalytic activity measurements, the Pt films were pretreated under H_2 at 400 °C for 1 h to reduce the metal.

Table 1
Experimental conditions for the catalytic reactions considered.

Reaction	Composition (%)/N_2 balance		
	CH_4	H_2O	O_2
Methane steam reforming (SRM)	1	4	0
Autothermal steam reforming (ATR)	1	4	0.2
Methane partial oxidation (MPO)	1	0	0.2

2.3. Characterization measurements

Several characterization techniques were used in order to investigate the different properties of the electrochemical catalysts. First, the macro-surface profile of the two different Pt catalyst-working electrode films was characterized using a perfilometer instrument (Veeco Dektak 150) and Vision 3-D analysis software. This technique allows obtaining a three-dimensional representative image (0.5 mm × 0.5 mm) of the surface of the prepared catalyst films. The morphology of the catalyst films was also investigated via scanning electron microscopy (SEM), using a FEI Nova NANOSEM 230 instrument. X-ray diffraction patterns of the two electrode films were recorded on a Philips PW 1710 instrument using Ni-filtered Cu Kα radiation.

In addition, in order to study the influence of the catalyst polarization on the tendency of carbon deposition under reaction conditions, in situ temperature-programmed oxidation experiments (TPO) were carried out for the electrochemical catalyst PPY. Before the TPO analysis, the reactor was purged under N_2, and it was cooled down to 250 °C. Then, a gas stream of 5% of O_2 under N_2 (total flow rate of 6 L h^{-1}) was fed to the reactor, and the temperature was increased at 5 °C/min to 600 °C. The amount of carbon previously deposited on the catalyst was evaluated by measuring the CO_2 concentration with a micro-gas chromatograph. The fast response of the micro-gas chromatograph for the CO_2 analysis allowed performing one analysis per minute.

3. Results and discussion

3.1. Influence of the preparation method of the catalyst film

In order to select the most suitable preparation method for the catalyst-working electrode film, both electrochemical catalysts (P and PPY) were tested for the SRM reaction under open circuit conditions and a fixed temperature of 500 °C (Fig. 1). Fig. 1a shows the variation of the specific hydrogen production rate (normalized per mass unit of Pt in order to compare the two electrochemical catalyst) versus time on the stream for both samples, whereas Fig. 1b shows the variation of the CO_2 selectivity and the methane conversion versus time for sample PPY. These reactions parameters were calculated as follows:

$$CH_4 \text{ conversion } (\%) = ([CH_4]_{in} - [CH_4]_{out})/[CH_4]_{in} \times 100 \qquad (3)$$

$$CO_2 \text{ selectivity } (\%) = [CO_2]_{out}/([CO]_{out} + [CO_2]_{out}) \times 100 \qquad (4)$$

where $[CH_4]_{in}$ corresponds to the methane concentration in the inlet reactor stream and $[CH_4]_{out}$, $[CO]_{out}$ and $[CO_2]_{out}$ denote the methane, carbon monoxide and carbon dioxide concentrations in the outlet stream, respectively.

It can be observed in Fig. 1a that the catalytic activity towards H_2 production of the two samples was almost the same at the beginning of the experiment. Nevertheless, a different deactivation trend was clearly observed. According to previous studies [32], the observed deactivation under SRM conditions was attributed to the formation of carbon which covers the catalytic active sites. It should be noted that this carbon deposition was experimentally evidenced by measuring CO_2 after purging the reactor with N_2 and subsequent switching to an O_2 stream (as will be shown later by TPO analysis). Hence, it can be observed that while the electrochemical catalyst P was deactivated after 1 h under reaction conditions, sample PPY exhibited an overall higher catalytic activity and was deactivated after 3 h. Then, it is clear that the addition of the 3% Pt/YSZ catalyst powder to the initial deposited Pt ink improved its resistance to deactivation. This fact can be attributed to the presence of Pt nanoparticles, which probably played an important role in the catalytic process and provided a higher number of active sites, as well as to the morphological modification of the structure of the film induced by the catalyst powder, as will be shown below.

On the other hand, it is interesting to note that sample PPY showed a good catalytic performance for H_2 production in view of its application for fuel cells. As shown in Fig. 1b, CO_2 selectivity was kept above 75% during the whole experiment, minimizing the undesirable production of CO. It can be attributed to a high catalytic activity of the electrochemical catalyst for the water gas shift reaction under the explored reaction conditions (reaction 2), which allowed to remove CO by the excess water and the further production of H_2. It can be explained by the low working temperature of the electrochemical catalyst (500 °C), which shifted the reaction 2 to the right [33]. However, in spite of the low operation temperature, the electrochemical catalyst showed a good performance for the H_2 production under the explored conditions, leading to an initial methane conversion higher than 45%. However, it is clear that after 3 h under reaction conditions, the system lost an important part of the activity due to carbon deposition. This fast deactivation, in comparison with that of Pt-dispersed catalysts [29], could be attributed to the typical low dispersion values of the catalyst-working electrode films used in NEMCA [14], hence leading to a rapid carbon blocking of the active sites. Nevertheless, as it will be shown in the next section,

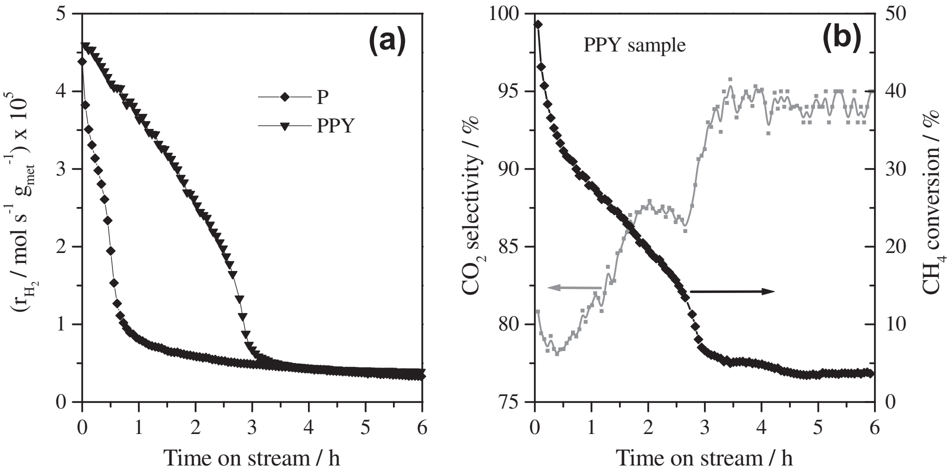

Fig. 1. Influence of the time on stream on the H_2 production rate (a) and on the methane conversion and CO_2 selectivity (b) for the different samples under SRM conditions at 500 °C.

this deactivation problem could be partially solved by the phenomenon of electrochemical promotion.

In order to explain the different catalytic behaviour of the two electrochemical catalysts (P and PPY), the morphology of the catalyst-working electrode films were characterized by different techniques. Fig. 2 shows the 3-D profiler image of catalyst-working electrode films (P and PPY). It can be clearly observed that sample PPY (Fig. 2b) exhibited a more homogeneous surface with a larger roughness and a higher number of valleys and holes in comparison with that of sample P (Fig. 2a). The addition of the Pt/YSZ catalyst powder allowed to re-disperse the Pt-painted film over a higher surface area (provided by the powder) during the calcination step, leading to a higher catalytic surface area and a lower Pt agglomerate size. This fact was confirmed by SEM analysis of both electrodes (Fig. 3). It can be observed that the conventionally painted sample (Fig. 3a) showed the typical big Pt agglomerates ranging from 0.5 to 1 μm [14]. However, the addition of the Pt/YSZ catalyst powder to the initial precursor slurry in sample PPY led to the formation of Pt particles with lower size (Fig. 3b). In order to complete the discussion, XRD analyses were also carried out over the Pt films for both samples (Fig. 4). The diffractograms showed peak assignments corresponding to Pt, according to JCPDS standards, which are consistent with a face-centred cubic (fcc) structure. No patterns of platinum oxides appeared in any of the samples. Additionally, sample PPY exhibited peaks at $2\theta \sim 30^\circ$, 35°, 50° and 63°, corresponding to YSZ patterns [34]. According to previous studies [35], one can estimate from the shape of the main Pt peak (1 1 1) and the Scherrer's equation [36] an overall value of the Pt crystal size. Thus, for sample P, a Pt particle diameter higher than 500 nm was measured, typically obtained for conventional Pt-painted films [14], whereas a much lower value (75 nm) was found for sample PPY. Apart from the approximate character of the technique, it is clear that the addition of the catalyst powder to the Pt-painted film strongly decreased the Pt particle size of the painted film and increased the dispersion of Pt particles. This observation is also in good agreement with the previous characterization techniques and supports the better catalytic performance of sample PPY compared to that of sample P. Thus, according to this preliminary study, all the catalytic experiments under closed circuit conditions (electrochemical promotion experiments) were henceforth carried out with sample PPY.

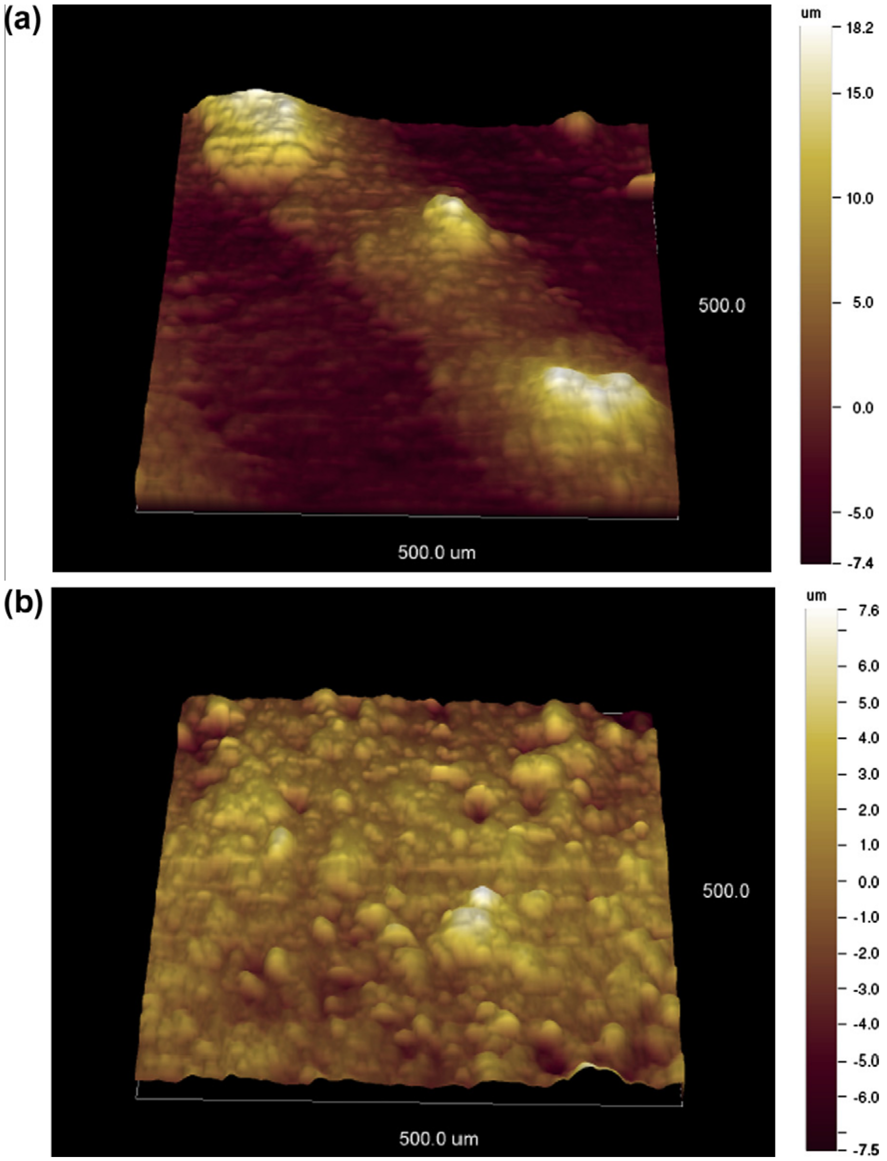

Fig. 2. High resolution 3-D profiler image of the Pt catalyst-working electrode of samples P (a) and PPY (b).

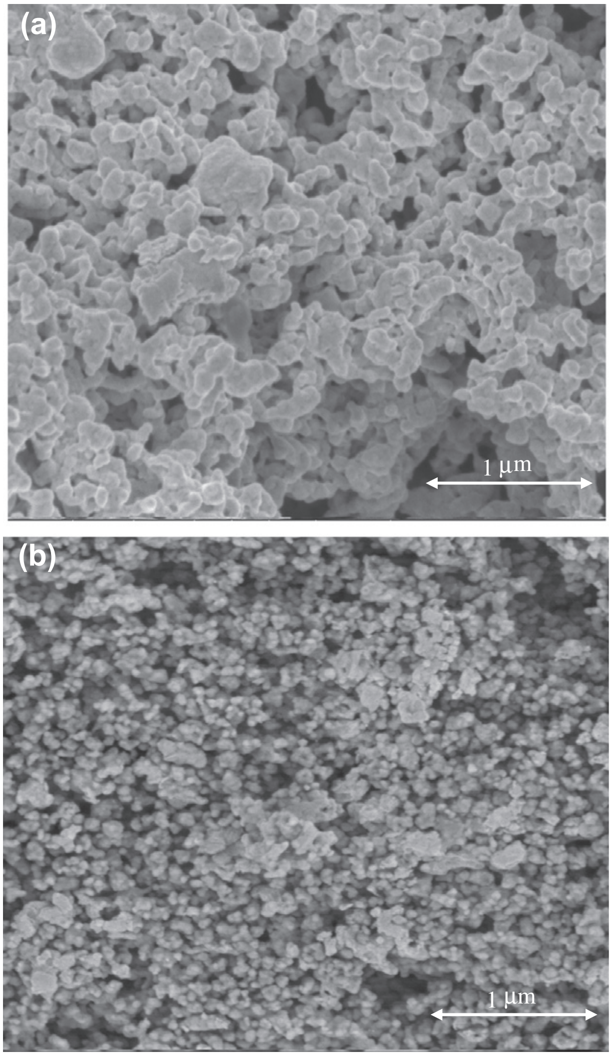

Fig. 3. SEM micrographs of the Pt catalyst-working electrode of samples P (a) and PPY (b).

3.2. Electrochemical promotion experiments

The phenomenon of electrochemical promotion provides a unique and remarkable way to modify the chemisorption properties of a catalyst under working reaction conditions [11–15]. It means that one can in situ control and modify under fixed reaction conditions the coverage of the different reactants species on the catalyst. Thus, it could be assumed that this phenomenon could be used for in situ regeneration of the catalyst from carbon deposition fragments, which is one of the main drawbacks of the reforming processes. In this sense, different electrochemical promotion experiments were carried out by applying polarizations to the solid electrolyte cell under different working conditions. Fig. 5 shows the variation of the hydrogen production rate versus time on stream under imposition of different potentials (for 1 h) for sample PPY under SRM conditions at 500 °C. Thus, it can be observed that initially at ($t = 0$), the system showed a high value of hydrogen production rate. However, during the subsequent positive polarizations ($V_{cell} = 2$, 1 and 0.5 V), the catalytic performance of the system strongly decreased due to the previously mentioned carbon deposition on Pt active sites. At this point, it should be mentioned that, considering the Pt film as the catalyst-working electrode of the cationic solid electrolyte cell, the application of these positive potentials would correspond to an unpromoted Pt surface, i.e., a catalyst surface clean of Na^+ promoting ions [37]. Then, under those positive potential conditions, the observed catalytic trend was almost the same as that observed in Fig. 1 under open circuit conditions, showing a pronounced deactivation with time on stream. However, it can be observed that the application of negative polarizations (e.g. $V_{cell} = -0.5$ V at $t = 3$ h) modified the catalytic trend of the system, leading to a slight increase in the H_2 reaction rate. One may rationalize the promotional phenomena observed with the cationic electrochemical catalyst on the basis of the electrode work function modification upon applied potential [38]. A decrease in the catalyst potential, and therefore, in the catalyst work function [11,14], led to an increase in the electronic density of Pt with a concomitant spillover of Na^+ ions from the electrolyte to the Pt surface. This work function decrease weakened the Pt chemical bonds with electron donor adsorbates and strengthened them with electron acceptors ones [39]. Under SRM conditions, the group of Prof. Vayenas [14,22] already identified the CH_4 as the electron donor species and H_2O as the electron acceptor ones. It implies that the subsequent decrease in the catalyst potential (from 2 V to −0.5 V) increased the coverage of OH (originating from H_2O chemisorption) on the catalytic sites, which partially removed the deposited carbon by gasification. This could explain the observed increase in the catalytic activity at −0.5 V.

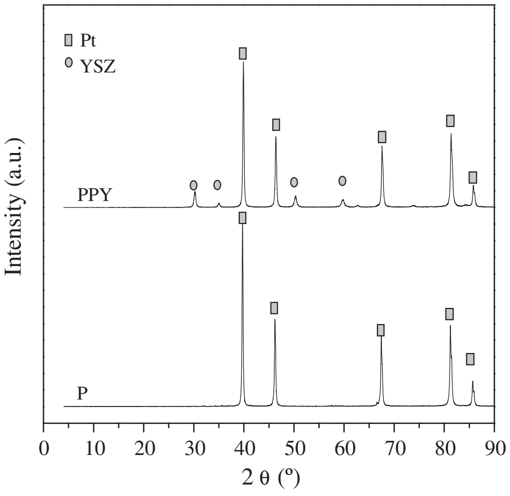

Fig. 4. XRD analysis of the catalyst-working electrode of samples P and PPY.

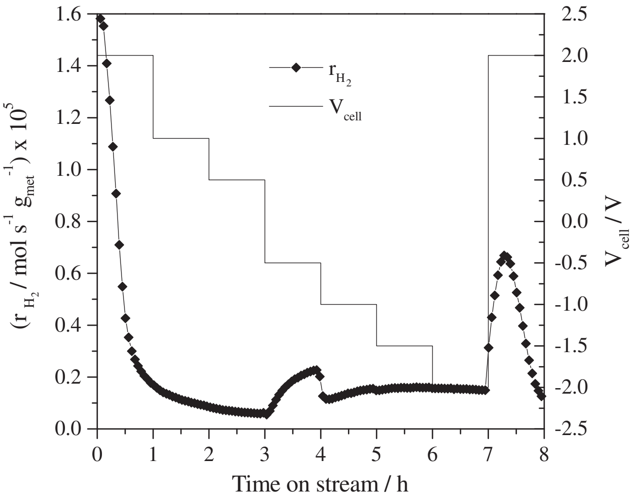

Fig. 5. Influence of the applied potential on the H_2 production rate under SRM conditions at 500 °C.

This observation is also in good agreement with previous studies with conventional dispersed catalyst, which have demonstrated that alkalis promote the activation of water, and hence the removal of hydrocarbon fragments under SRM conditions [29,30,40]. However, it can be observed that the H_2 production rate at $V_{cell} = -0.5$ V was lower than the initial one at $V_{cell} = 2$ V. It can be attributed, according to the previous explanation, to the low CH_x (originating from CH_4 chemisorption) coverage under the application of negative polarizations. It should be noted that under positive polarization, there is a high CH_x coverage, which would explain not only the higher H_2 formation but also the fast initial deactivation. This explanation is also in good agreement with a previous study performed on Pt/YSZ-dispersed catalyst [40]. A lower activity was reported for the alkali-modified catalyst during SRM on Pt/YSZ in comparison with that of clean alkali Pt surface. This fact was attributed to a low coverage of CH_x species in the alkali promoted catalyst, which also supports the idea that the CH_4 dissociative adsorption is the rate-determining step of the process [28]. On the other hand, it can be observed that the subsequent application of a more negative potential ($V_{cell} = -1$ V) decreased the catalytic activity of the system, which can be attributed to an excess of Na^+ ions on the catalyst film and to subsequent formation of sodium-derived compounds, which, in turn, probably blocked the Pt active sites [41]. However, the most interesting part of the figure comes from the last application of a positive potential of 2 V. It led to an important initial increase in the catalytic activity of the system, in spite of its deactivation, due to the carbon deposition. In good agreement with the previous explanation, the application of a positive potential again increased the chemisorption of CH_x species, enhancing the production of H_2 but leading to a fast deactivation due to the low coverage of water (OH species) responsible from the removal of carbon. It can also be observed that the maximum value for the H_2 production rate during this second application of $V_{cell} = 2$ V was almost the half in comparison with the first application of this potential. This fact demonstrates that the enhancement of the chemisorption of water-derived species under SRM conditions and under the application of negative potential only allowed to partially regenerate the catalyst from carbon deposition fragments.

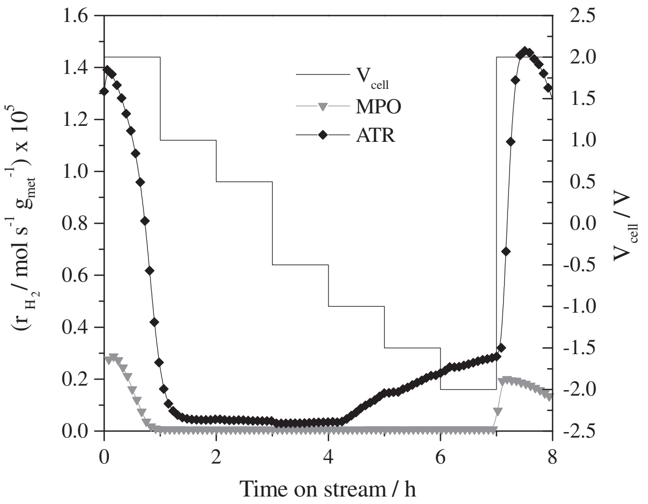

Fig. 6. Influence of the applied potential on the H_2 production rate under ATR and MPO conditions at 500 °C.

In order to select a more suitable atmosphere for the application of the NEMCA effect on these H_2 production processes, the same experiment was repeated at 500 °C under autothermal steam reforming conditions (ATR) and under methane partial oxidation conditions (MPO), according to the compositions listed in Table 1. Fig. 6 shows the variation of the H_2 production rate versus time on stream during the imposition of different potentials under both atmospheres. First, it can be observed by comparing the overall H_2 production rates under all the explored atmospheres (Figs. 5 and 6) that the presence of O_2 in the ATR conditions led to a slightly lower H_2 production rate value, probably due to the partial consumption of H_2 with O_2 from the gas phase. In addition, the much lower H_2 production rates found under MPO conditions (Fig. 6b) in comparison with that under ATR conditions (Fig. 6a) would demonstrate that the major part of H_2 was produced via the reforming mechanism versus the partial oxidation one. However, the most interesting point of the figure comes from the complete regeneration of the catalyst under the application of a negative polarization. This fact, very clear under ATR conditions, indicates that the presence of O_2 in the gas phase led to a complete regeneration of the catalyst under negative polarizations (in comparison with SRM conditions, shown in Fig. 5). Under ATR conditions, the second application of the positive potential led to the same catalytic performance as that observed in the first polarization at 2 V. This could be due to the stronger electron acceptor character of O_2 respect to the other reactants [14,17,31,35]. Thus, the application of the negative polarization led to a strong increase on the chemisorption of electron acceptor species, in this case mainly O_2, which efficiently removed the previously deposited carbon.

The above discussion can be supported by TPO analysis (Fig. 7) carried out for sample PPY under open circuit conditions and after treating it as follows:

(a) ATR conditions for 2 h under application of 2 V.
(b) ATR conditions for 2 h under application of 2 V and subsequent treating under ATR conditions during 4 h at −1 V.

Fig. 7 shows two different CO_2 peaks, which could be attributed to the presence of two different kinds of carbon deposited on the catalyst surface [42] or the removal of the deposited carbon from two different kinds of Pt active sites, which favoured the carbon combustion at different temperatures. Anyway, from the TPO profiles, it can be observed that the total amount of carbon was much lower after working under negative polarization than for the catalyst film that only worked under positive polarization. This fact would demonstrate, for the first time in literature, the possibility of electrochemically regenerating the catalyst under fixed reaction

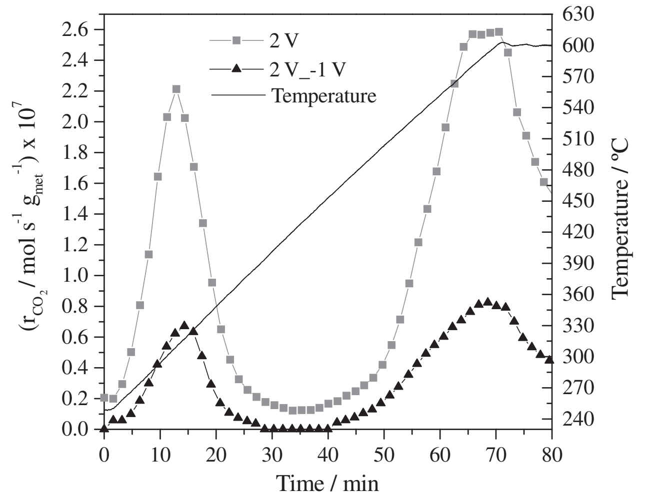

Fig. 7. TPO analysis of sample PPY: (a) after 4 h under ATR conditions with application of 2 V and (b) after 4 h under ATR conditions with application of 2 V and subsequent treating for 4 h under ATR conditions at −1 V.

conditions using a cationic solid electrolyte support. At this point, it should be mentioned that a similar electrochemical regeneration of carbon deposition fragments was observed by the group of Prof. Vayenas [22] using a Ni/YSZ electrochemical catalyst under SRM. In this case, under carbon deposition conditions, the application of anodic potential and hence the electrochemically supply of O^{2-} ions to the catalyst film, allowed to partially remove carbon under SRM conditions with the subsequent increase in the catalytic activity. However, as already mentioned, the new electrochemical catalyst developed in this work allowed to additionally work at low temperatures with a low CO production, which is interesting in view of its application in fuel cells.

Next, in order to check the reproducibility of different regeneration cycles, a long time reaction experiment under polarization was carried out. Fig. 8 shows the variation of H_2, CO and CO_2 production rates with time on stream under different cycles of positive and negative potentials under ATR conditions. In this experiment, a negative potential of −1 V was applied for 4 h and then a positive polarization of 2 V was applied for 2 h. In agreement with the previous figure, it can be observed that the system could be electrochemically regenerated during the negative polarization at −1 V, while the positive application of 2 V would yield to an important H_2 production rate. This system showed a reproducible behaviour along the different cycles, being attributed the slight differences observed in the figure to the non-continuous mode of analysing of the micro-gas chromatograph. It is clear that the phenomenon of electrochemical promotion could be used to regenerate, in principle, in an unlimited way, the catalytic performance of the system for the low-temperature H_2 production from CH_4. It would imply a new advantage of the electrochemical catalyst when compared to the conventional one. For instance, previous studies under ATR conditions [32,43] have shown an important deactivation problem of Pt-based catalyst. Then, the possibility of in situ electrochemical regeneration of a catalyst in a reversible way would imply an important technological advance of the phenomenon of electrochemical promotion. In addition, this regeneration could be carried out under fixed reaction conditions, which would avoid the need of modifying the reaction atmosphere as it happens with conventional catalysts. On the other hand, it is also interesting to remark again the low tendency of the system to produce CO, being the average CO_2 selectivity values higher than 95% during the whole experiment.

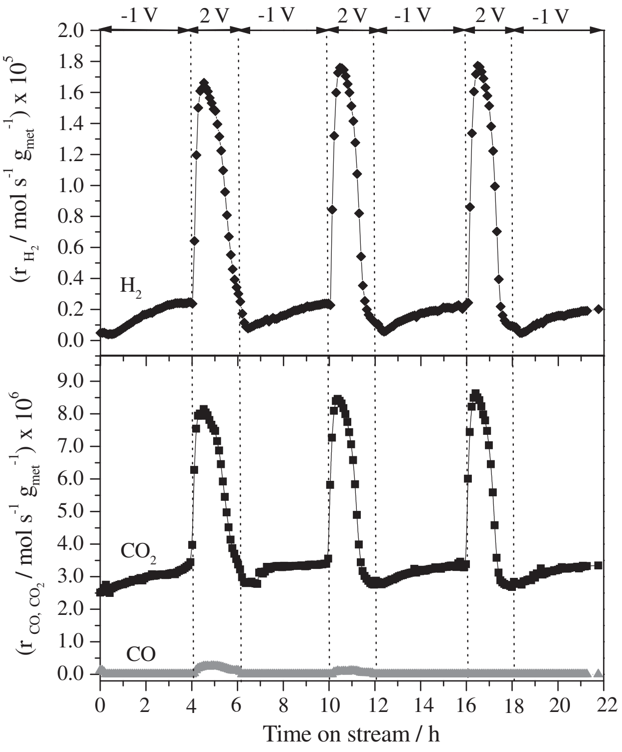

Fig. 8. Influence of the applied potential on the H_2, CO and CO_2 production rates during the reproducibility experiment under ATR conditions at 500 °C.

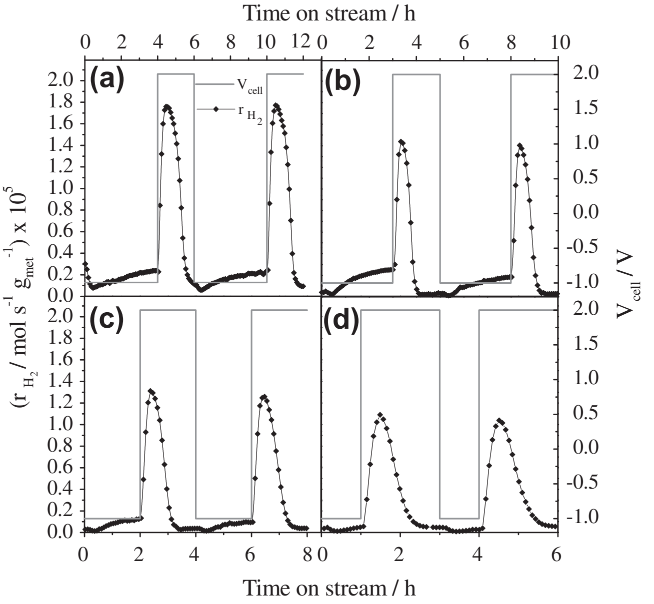

Fig. 9. H_2 production rate variation versus time on stream under different regeneration cycles at negative potential under ATR conditions.

Finally, in order to investigate the influence of the regeneration time on the catalytic performance of the system, different reproducibility experiments were carried out by varying the negative polarization regeneration time. Fig. 9 shows the variation of the H_2 production rate versus time on stream under different cycles of positive and negative polarization. In this figure, the time of positive polarization was fixed in 2 h, while the regeneration time at negative polarization was varied from 4 to 1 h (Fig. 9a–d). It is clear that the catalytic performance of the system during the positive polarization strongly depended on the negative polarization regeneration time. Thus, as the negative polarization time increased, the system deactivated later during the subsequent positive polarization, leading to a more reproducible behaviour, and produced high amount of H_2. For instance, the application of a negative polarization for 4 h (Fig. 9a) led to a completely reproducible behaviour between the two cycles, which would indicate that most of the deposited carbon in the first cycle has been removed. However, the application of the negative potential for less than 4 h (Fig. 9b–d) led in the second cycle to a slight decrease in the catalytic performance of the system, indicating that not all the carbon was removed. Thus, according to the reproducibility behaviour of the system, 4 h seems to be the minimum regeneration time for a complete removal of the carbon deposited on the catalyst at the negative potential of −1 V.

4. Conclusions

Different conclusions of theoretical and practical importance can be obtained from this work where a cationic electrochemical catalyst has been developed for low-temperature H_2 production processes:

- The addition of a catalyst powder (3% Pt/YSZ) to the Pt-painted film strongly improved its catalytic performance by increasing the overall dispersion of the film and the surface contact area with the reactive gas phase.

- The developed electrochemical catalyst (Pt–Pt/YSZ/Na–βAl_2O_3) allowed producing H_2 from methane at low temperature with suitable values of conversion and extremely high values of CO_2 selectivity.
- The phenomenon of electrochemical promotion allowed to electrochemically regenerate the catalyst film from carbon deposition fragments by increasing the coverage of O_2- and H_2O- derived species (electron acceptor molecules) under negative polarization. The possibility of electrochemically controlling the amount of produced H_2 free of CO under fixed conditions could be very interesting from a technological point of view (on-board H_2 production for automotives).
- The most efficient H_2 production process for application of NEMCA with a cationic solid electrolyte was the autothermal reforming reaction. The presence of O_2 in the gas phase allowed the complete regeneration of the catalyst under negative polarization, in a reproducible way.

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