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# Regeneration study of Ni/hydroxyapatite spent catalyst from dry reforming

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## ABSTRACT

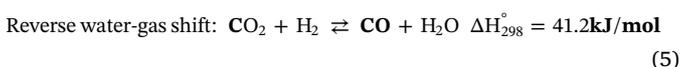
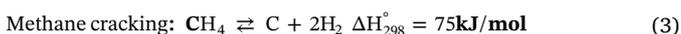
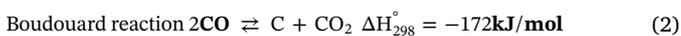
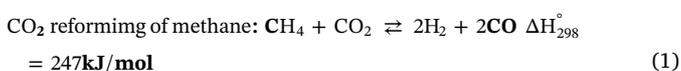
In the present work, the regeneration of a spent nickel hydroxyapatite-based catalyst (Ni/Ca-HA1\_S) used in dry reforming of methane (DRM) was investigated. Three successive cycles of DRM/regeneration were performed. Two different gasifying agents were tested for the regeneration step: air and carbon dioxide (21%CO<sub>2</sub>/N<sub>2</sub>). The aim was to evaluate the ability of regeneration of the catalyst under different atmospheres. The regeneration was performed *in situ* at 700 °C under 70 mL/min of gasifying agent. Reproducible results were obtained between each cycle for the two atmospheres tested and only a small irreversible deactivation was noticed. Several characterizations (SEM, TEM, TPR, XRD) of the fresh and spent catalysts allowed proving that the irreversible deactivation was provoked by densification of nickel particles and core-shell carbon formation. Despite the slight decrease in reactants' conversions, selectivity to syngas was around 80–90% during the three cycles of DRM/regeneration with both atmospheres and no changes in the selectivity were observed. The results proved that the Ni/Ca-HA1\_S catalyst could be easily regenerated under different atmospheres and make it competitive for dry reforming of methane.

### Keywords:

hydroxyapatite  
dry reforming of methane  
nickel catalyst  
syngas  
catalyst regeneration

## 1. Introduction

Carbon dioxide (CO<sub>2</sub>) reforming of methane (CH<sub>4</sub>) (Eq. (1)) has gained increasing attention due to the conversion of two main greenhouse gases into syngas (mixture of hydrogen and carbon monoxide), which can further be used in the production of energy and of high-value added chemicals [1–3]. Nickel-based catalysts have been extensively investigated for this process due to its high catalytic activity in this reaction. However, they undergo severe deactivation due to catalyst sintering under the high temperatures required for the reaction and mostly due to coke deposition over the active sites of the catalyst [4,5]. In fact, many parallel reactions occur along with the dry reforming reaction (DRM) (Eq. (2)–(5)) and coke can originate from many of these reactions (Eq. (2)–(4)).



So, in the past few years, many studies have focused on the improvement of the physico-chemical properties of the catalysts and on the optimization of the reaction conditions in order to obtain high catalytic conversion and stability during long periods of time [6]. They include the use of basic promoters, of supports with oxygen storage capacity, the combination of different transition metals, the optimization of preparation pathways of the catalysts etc [7–19]. Also, temperature, pressure, reactants ratio and type of reactor have been investigated [10,20,21].

Nevertheless, the capacity of regeneration of the catalysts is also an important parameter. The regeneration process allows cleaning the coke deposit from the surface and the pores of the catalyst without destroying or modifying the structure of the catalyst [7]. This aspect has economic and environmental impact. In fact, the costs of regeneration should remain lower than the costs of obtaining fresh catalysts [7]. Moreover, regenerating the catalyst instead of disposing it as solid waste is an environmentally friendly option since the spent catalyst can form toxic metal compounds in the environment [22]. So, regeneration studies of spent catalysts have also been conducted aiming to re-use the deactivated catalysts.

Vicerich et al. [23] investigated the regeneration with oxygen diluted in nitrogen at 450–550 °C of the PtReIn/Al<sub>2</sub>O<sub>3</sub> catalyst used in cyclohexane dehydrogenation and cyclopentane hydrogenolysis. They showed that the regeneration process could fully recover the activity of the spent catalyst. Wu et al. [15] showed that the regeneration at 300 °C

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of the Rh<sub>0.1</sub>Ni<sub>10</sub>/BN catalyst could remove the carbon deposit and reactivate the catalyst, but a small decrease in the activity was observed. Simson et al. [24] investigated the regeneration of a Pt/Rh catalyst after steam reforming of an ethanol/gasoline mixture. They showed that thermal treatment under air could fully restore the performance of the catalyst. However, after regeneration, their catalyst deactivated more quickly than the fresh one. Similarly, Sanchez et al. [25] reported that the catalytic performance of their reforming catalyst could be recovered by air combustion of the coke deposits but its selectivity to H<sub>2</sub> quickly decreased.

Most of the literature reports on catalyst regeneration are related to the combustion of coke with air due to its availability. Also, the mechanism of carbon species oxidation by O<sub>2</sub> has been widely investigated. There are many references in the literature to carbon bulk diffusion through the metal particle, oxygen spillover and redox mechanism [26]. However, coke deposits can be eliminated not only by O<sub>2</sub> but also by different gasifying agents, such as steam and CO<sub>2</sub> [27]. There are only few studies that investigated the effect of other gasifying agents such as CO<sub>2</sub> on the regeneration of catalysts [28] and the mechanism of carbon removal by these gases is not yet well known [26].

Hydroxyapatite has been investigated as catalyst support in many different reactions such as water gas shift [29], partial oxidation of methane [30], steam reforming of glycerol [31] etc. In fact, hydroxyapatite can undergo substitutions in its crystal lattice, which may favor the incorporation of an active phase to the catalyst [32,33]. Also, this material present high chemical and thermal stability, it has very low solubility in water and it does not sinter at temperatures lower than 700 °C [34,35]. Moreover, it presents basic sites that can reversibly adsorb carbon dioxide and help coke removal [36]. Despite all these advantages, only few works has been published using hydroxyapatite as catalyst for dry reforming of methane reaction. We have previously demonstrated that hydroxyapatite-based catalysts were performing for dry reforming of methane reaction [37,38]. So, in the present work, Ni/hydroxyapatite catalyst was investigated in CO<sub>2</sub> reforming of CH<sub>4</sub> reaction, with a focus on the regeneration process of the deactivated catalyst. The effect of gasifying agent on the re-use of the catalyst was also investigated by using two different gasifying agents: air and carbon dioxide. CO<sub>2</sub> was used in this work because it is one of the reactants of DRM and the reaction between CO<sub>2</sub> and solid carbon (Boudouard reaction, Eq. (2)) produces CO, which is one of the products of DRM. Also, the basic properties of the hydroxyapatite could favor the CO<sub>2</sub> adsorption and consequently, solid carbon (C<sub>(s)</sub>) gasification. The objective of this work was to evaluate the reproducibility of the performance of the Ni/hydroxyapatite catalyst under several reaction/regeneration cycles and under different regeneration atmospheres.

## 2. Materials and methods

### 2.1. Catalyst preparation

The hydroxyapatite (Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>) support used in this work was provided by PRAYON. Besides coke deposition, one of the reasons for catalyst deactivation is the support sintering [7]. So, as in this work the DRM reaction is performed at mild temperature (700 °C), the hydroxyapatite support was previously sintered at 1000 °C for 5 h at 10 °C/min to ensure support stability during the catalytic tests and to avoid later catalyst deactivation by support sintering. The catalyst was prepared by incipient wetness impregnation method by impregnating the support with an aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Fisher Scientific, > 98 wt%). The amount of nickel on the catalyst was 5.7 wt.%. Then the catalyst was dried at 105 °C overnight. The catalyst was referred to as Ni/Ca-HA1\_S. In order to obtain more precise characterization results of nickel particles on the catalyst during the reaction, a calcination step under air at 500 °C was performed for two hours before XRD, SEM and TEM analyses.

### 2.2. Dry reforming of methane

The dry reforming of methane was carried out in a fixed-bed tubular reactor with inner diameter of 8 mm 300 mg of the catalyst was diluted 2 times with inert alumina powder to improve heat exchange inside the catalyst bed. The same alumina was used to place the catalyst at the center of the reactor. The pressure drop in the reactor was 1.6 bar. The temperature of the reaction was controlled by a thermocouple placed at the center of the catalyst bed. The catalyst was reduced *in situ* at 700 °C for 2 h under 4%H<sub>2</sub>/N<sub>2</sub> flow (70 mL/min). Then, DRM was carried out for 30 h at 700 °C with a WHSV of 15882 mL h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> with a synthetic gas mixture containing 20% of CH<sub>4</sub>, 20% of CO<sub>2</sub> and 60% of N<sub>2</sub> (volume percentage). A silica gel tube was used as water trap at the reactor outlet. Quantification of the water produced during the reaction was made by mass difference of this water trap. Also, a gas counter was used for the measurement of the total gas flow rate at the reactor outlet. The measure of the total gas flow rate at the reactor outlet allowed taking into account the change in the total number of moles between reactants and products to calculate the composition at the reactor outlet. Gas products were analyzed by a μ-GC A3000 (Agilent) equipped with a thermal conductivity detector (TCD).

Methane and carbon dioxide conversion and products selectivity were calculated as follows:

$$\text{CH}_4\text{conversion}(\%) = (\dot{Q}_{(\text{CH}_4)_{\text{in}}} - \dot{Q}_{(\text{CH}_4)_{\text{out}}}) / (\dot{Q}_{(\text{CH}_4)_{\text{in}}}) \times 100 \quad (6)$$

$$\text{CO}_2\text{conversion}(\%) = (\dot{Q}_{(\text{CO}_2)_{\text{in}}} - \dot{Q}_{(\text{CO}_2)_{\text{out}}}) / (\dot{Q}_{(\text{CO}_2)_{\text{in}}}) \times 100 \quad (7)$$

$$\text{H}_2\text{Oselectivity}(\%) = (\dot{Q}_{(\text{H}_2\text{Oproduced})}) / (\dot{Q}_{(\text{O}(\text{CO}_2\text{consummed})})} \times 100 \quad (8)$$

$$\text{COselectivity}(\%) = (\dot{Q}_{(\text{O}(\text{COproduced})})} / (\dot{Q}_{(\text{O}(\text{CO}_2\text{consummed})})} \times 100 \quad (9)$$

$$\text{H}_2\text{selectivity}(\%) = (\dot{Q}_{(\text{H}(\text{H}_2\text{produced})})} / (\dot{Q}_{(\text{H}(\text{CH}_4\text{consummed})})} \times 100 \quad (10)$$

$$\text{C}_{(s)}\text{selectivity}(\%) = (\dot{Q}_{\text{C}_{(s)}(\text{out})}) / (\dot{Q}_{\text{C}(\text{CH}_4\text{consummed})} + \dot{Q}_{\text{C}(\text{CO}_2\text{consummed})}) \times 100 \quad (11)$$

where  $\dot{Q}_{(\text{CH}_4)_{\text{in}}}$  and  $\dot{Q}_{(\text{CH}_4)_{\text{out}}}$ : methane molar flow rate (mmol h<sup>-1</sup>) at the reactor inlet and outlet;  $\dot{Q}_{(\text{CO}_2)_{\text{in}}}$  and  $\dot{Q}_{(\text{CO}_2)_{\text{out}}}$ : carbon dioxide flow rate (mmol h<sup>-1</sup>) at the reactor inlet and outlet;  $\dot{Q}_{(\text{H}_2\text{Oproduced})}$ : atomic oxygen flow rate (mmol h<sup>-1</sup>) at the reactor outlet (under H<sub>2</sub>O form);  $\dot{Q}_{(\text{O}(\text{CO}_2\text{consummed})})}$ : atomic oxygen flow rate (mmol h<sup>-1</sup>) (under form of CO<sub>2</sub> consumed);  $\dot{Q}_{(\text{O}(\text{COproduced})})}$ : atomic oxygen flow rate (mmol h<sup>-1</sup>) at the reactor outlet (under CO form);  $\dot{Q}_{(\text{H}(\text{H}_2\text{produced})})}$ : atomic hydrogen flow rate (mmol h<sup>-1</sup>) at the reactor outlet (under H<sub>2</sub> form);  $\dot{Q}_{(\text{H}(\text{CH}_4\text{consummed})})}$ : atomic hydrogen flow rate (mmol h<sup>-1</sup>) (under form of CH<sub>4</sub> consumed);  $\dot{Q}_{\text{C}_{(s)}(\text{out})}$ : solid carbon flow rate at the outlet of the reactor deduced from mass balance.

The reaction/regeneration cycles were carried out as follows:

a) Activation of the catalyst at 700 °C under 4%H<sub>2</sub>/N<sub>2</sub> was performed for 2 h. The dry reforming reaction was carried out at 700 °C for 30 h as previously explained. After the reaction, the reactive gases were switched with air. The temperature was kept at 700 °C and 70 mL/min of air flowed through the catalyst for 1h30 min. During the regeneration process, the concentration of CO<sub>2</sub> resulting from the oxidation of coke was monitored by a gas chromatography.

b) Activation of the catalyst at 700 °C under 4%H<sub>2</sub>/N<sub>2</sub> was performed for 2 h. The dry reforming reaction was carried out at 700 °C for 30 h as previously explained. After the reaction, the reactive gases were switched to a gas mixture containing 21% of CO<sub>2</sub> and 79% of N<sub>2</sub> (volume percentage). The temperature was kept at 700 °C and 70 mL/min of the gas mixture flowed through the catalyst for 1h30 min. During the regeneration process, the concentration of CO resulting from the oxidation of coke was monitored by gas chromatography.

Three cycles of DRM/regeneration for both gasifying agents were performed to test the regeneration capacity of the hydroxyapatite catalyst under different atmospheres.

### 2.3. Characterization

$N_2$  adsorption isotherms were recorded with a Micromeritics Tristar II 3020 to evaluate the specific surface area and the pore volume of the support and of the fresh catalyst. BET surface area was calculated from the nitrogen adsorption isotherms. Prior to the analyses, the samples were outgassed at 105 °C for 24 h at low pressure (< 100 mbar).

Carbon dioxide temperature-programmed desorption ( $CO_2$ -TPD) was performed on a Micromeritics AutoChem 2920 Analyzer equipped with a thermal conductivity detector (TCD) to evaluate the basicity of the hydroxyapatite support. 100 mg of the support was pretreated at 800 °C (10 °C/min) under helium flow and then it was cooled to 50 °C at 10 °C/min. Then, the sample was saturated with 0.5%  $CO_2/N_2$  (15 mL/min) for 30 min. Afterwards, 25 mL/min of He were flushed for 30 min to eliminate physisorbed  $CO_2$  molecules. TPD was finally recorded from 50 to 800 °C at a heating rate of 10 °C/min.

X-ray diffraction (XRD) was carried out using a Phillips Panalytical X'Pert MPD diffractometer operating with Cu  $K\alpha$  radiation ( $\lambda = 1.543 \text{ \AA}$ ) over a  $2\theta$  range of 10–75° and scan step size of  $0.042^\circ s^{-1}$ . Prior to the analyses, the catalyst was calcined at 500 °C under air.

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) analyses were performed with a HORIBA Jobin Yvon Ultima 2 apparatus to evaluate the Ni content in the catalyst sample. Prior to the measurements, 100 mg of the hydroxyapatite-based catalysts were dissolved in aqua regia (33vol%  $HNO_3$  + 67vol%  $HCl$ ) and heated at 90 °C for 1 h.

Environmental Scanning Electron Microscopy (ESEM) analysis was performed of a Philips XL30 ESEM FEG to characterize the shape and size of support and metal particles.

Transmission electron microscopy (TEM) images of fresh and spent catalyst were recorded on a MET JEOL ARM200F. Prior to the analyses, the catalysts were calcined at 500 °C under air atmosphere.

Temperature-programmed reduction (TPR) profiles of the dried catalysts were recorded with a Micromeritics AutoChem 2920 Analyzer in the temperature range of 25–850 °C. 100 mg of the sample was placed in a quartz reactor and reduced by a 5%  $H_2/N_2$  gas mixture with a heating rate of 10 °C/min. Prior to the analysis, the sample was purged under pure helium at 100 °C for 30 min to clean the surface of the sample.

## 3. Results and discussion

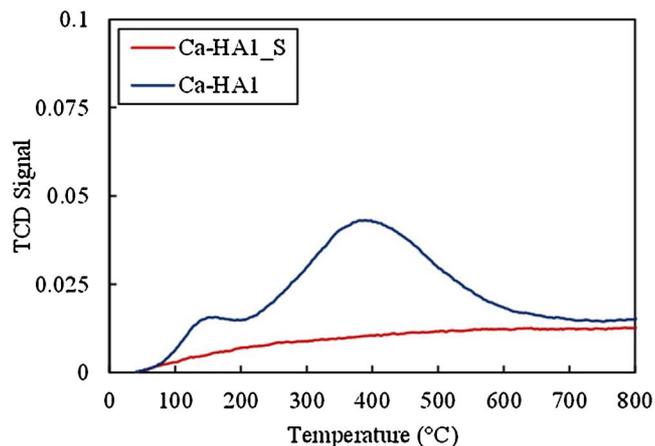
### 3.1. Characterization of samples

#### 3.1.1. Physico-chemical properties of support and catalyst

Table 1 depicts the specific surface area ( $S_{BET}$ ), pore volume ( $V_p$ ) and nickel amount of the Ca-HA1\_S support and of the Ni/Ca-HA1\_S catalyst. For the purpose of comparison, the  $S_{BET}$  and the  $V_p$  of the hydroxyapatite support before thermal treatment (Ca-HA1) is also shown. The initial hydroxyapatite presented 7  $m^2/g$  of specific surface area and negligible pore volume. As expected, the hydroxyapatite support (Ca-HA1\_S) and the Ni/Ca-HA1\_S catalyst presented very low specific surface area and pore volume. In fact, sintering took place during thermal treatment at high temperature, which resulted in the loss of surface area and porosity. The addition of nickel to the support

**Table 1**  
Physico-chemical properties of support and catalyst.

Sample	Textural characterization		ICP-OES
	$S_{BET}$ ( $m^2/g$ )	$V_p$ ( $cm^3/g$ )	Ni wt.%
Ca-HA1	7	nd	–
Ca-HA1_S	< 3	$\approx 0$	–
Ni/Ca-HA1_S	< 3	$\approx 0$	4



**Fig. 1.**  $CO_2$ -TPD of hydroxyapatite support before (– Ca-HA1) and after thermal treatment (– Ca-HA1\_S).

did not modify its specific surface area. The nickel loss was related to the fixation of the metal on the flask wall during the impregnation step.

#### 3.1.2. $CO_2$ -Temperature programmed desorption ( $CO_2$ -TPD)

$CO_2$ -TPD was conducted to evaluate the density and the strength of basic sites of the Ca-HA1\_S support in order to evaluate the influence of the hydroxyapatite support on the performance of the catalyst. The density of basic sites is represented by the area under the curves and the strength of the sites is represented by the temperature of desorption. High temperatures represent strong basic sites. For comparison, the hydroxyapatite before thermal treatment (Ca-HA1) was also evaluated. Fig. 1 presents the  $CO_2$ -TPD curves of this support.

The hydroxyapatite before thermal treatment (Ca-HA1) presented a small peak centered at about 150 °C and a broad peak between 200 and 600 °C. The desorption peaks of this material covered a wide range of temperature, which indicated the presence of weak, medium and strong basic sites. The thermal treatment completely changed the basicity of the initial hydroxyapatite. No desorption peaks were observed for the Ca-HA1\_S support, which indicated that the basicity of this support was negligible after thermal treatment. In fact, the thermal treatment led to a full densification of the hydroxyapatite and destroyed its surface functions.

#### 3.1.3. XRD analysis

XRD patterns of support and catalyst is shown in Fig. 2.

Both support and catalyst showed the presence of the hydroxyapatite phase ( $Ca_{10}(PO_4)_6(OH)_2$ ) with the main peaks at 31.9°, 32.3°, 33.0° and 34° (pattern number: COD 96-230-0274). Comparison between XRD patterns of the support before (Fig. 2a) and after (Fig. 2b) thermal treatment indicated that the thermal treatment of the hydroxyapatite did not change its structure, only its crystallinity. Besides the hydroxyapatite phase, the Ni/Ca-HA1\_S catalyst also presented a NiO phase with main diffraction peaks at 37°, 43° and 63°. No peaks of Ni-exchanged hydroxyapatite were detected, which suggested the nickel was mainly located on the surface of the hydroxyapatite and not in its structure.

#### 3.1.4. SEM and TEM analyses

Fig. 3 shows the SEM images of the Ca-HA1\_S support and of the Ni/Ca-HA1\_S fresh catalyst.

Fig. 3a shows the SEM image of the hydroxyapatite support after the thermal treatment. A coalescence of the hydroxyapatite particles could be observed, indicating the sintering of this material. Fig. 3b shows the SEM image of the Ni/Ca-HA1\_S catalyst. Large nickel particles of about 100–200 nm could be observed. However, SEM analysis is not precise enough to indicate if each particle observed is only one nickel particle

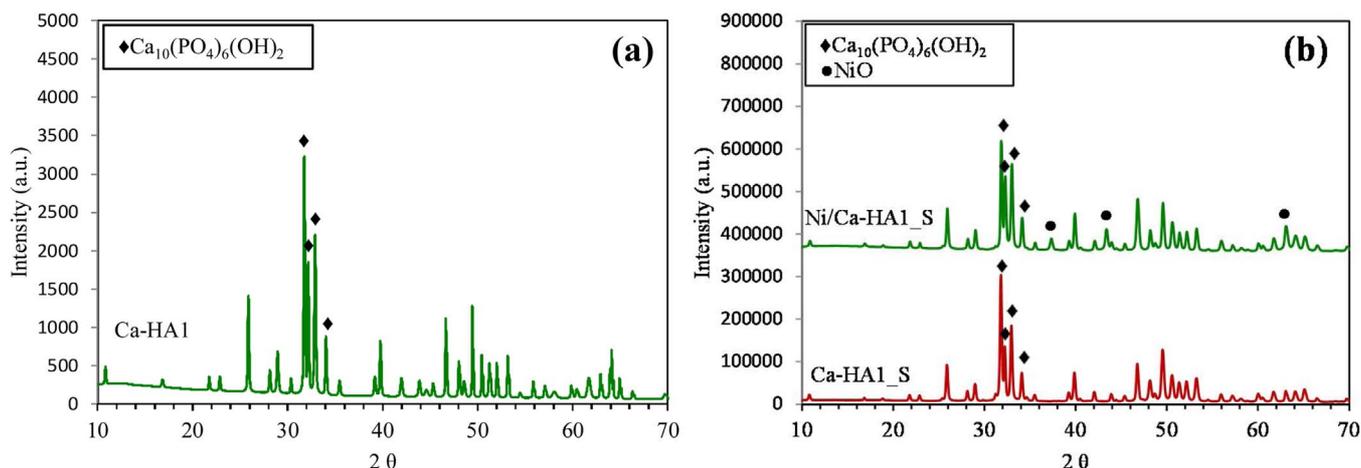


Fig. 2. XRD patterns of (a) Ca-HA1 support before thermal treatment and of (b) Ca-HA1\_S support (after thermal treatment) and of Ni/Ca-HA1\_S catalyst.

or an agglomerate.

To confirm the SEM results, TEM analysis was performed. Fig. 4 illustrates the TEM images of the fresh Ni/Ca-HA1\_S catalyst.

TEM analysis showed the presence of large nickel particles with sizes between 100 and 200 nm. Also, the nickel particles observed are porous and have square shape (2D), which corresponded to the cubic structure of NiO [2,19,39].

### 3.1.5. TPR analysis

TPR analysis was performed to evaluate the reducibility of the Ni/Ca-HA1\_S catalyst. Fig. 5 shows the TPR curve of this catalyst.

Ni/Ca-HA1\_S catalyst presented two reduction peaks centered at 395 and 402 °C. According to Ahmed et al. [40] and Wu et al. [41], these peaks correspond to the reduction of NiO species with different oxidation degrees located at the external surface of the support and weakly interacting with the support. This result confirms the XRD analysis.

## 3.2. Catalyst behavior under DRM/regeneration cycles

### 3.2.1. Catalytic performance under DRM/Air-regeneration cycles

Fig. 6 shows the evolution with time on stream (TOS) of the CH<sub>4</sub> and CO<sub>2</sub> conversions as well as of the H<sub>2</sub>, CO, H<sub>2</sub>O and solid carbon (C<sub>(s)</sub>) selectivities for the Ni/Ca-HA1\_S catalyst under three successive cycles of DRM/Air regeneration.

In the first cycle (blue dots), the Ni/Ca-HA1\_S catalyst showed high CH<sub>4</sub> and CO<sub>2</sub> conversion around 70% that decreased to 52% and 61%,

respectively during 30 h of TOS. H<sub>2</sub> and CO selectivity were constant at around 90%. As consequence, low H<sub>2</sub>O and C<sub>(s)</sub> were obtained. H<sub>2</sub>O selectivity was constant at around 10% and C<sub>(s)</sub> was lower than 10%. The deactivation of the catalyst was probably related to coke deposition (Eq. 2-4) and/or catalyst sintering. The catalyst presented initially good activity and stability on DRM for 30 h of TOS, showing that the hydroxyapatite-based catalyst was performing for this reaction. This proves that the physical properties (low S<sub>BET</sub> and V<sub>p</sub>, Table 1) are compensated by its chemistry.

After *in situ* regeneration by coke combustion under air flow and reactivation under 4%H<sub>2</sub>/N<sub>2</sub> flow, the catalyst exhibited similar performance as in the first cycle, showing only a small decrease in CH<sub>4</sub> and CO<sub>2</sub> conversions (red dots). This suggested that irreversible deactivation caused by catalyst sintering took place. CH<sub>4</sub> and CO<sub>2</sub> conversions were initially around 60 and 70% and decreased to 47 and 56%, respectively during 30 h of TOS. However, H<sub>2</sub> and CO selectivities were constant at about 90% during the test, as in the first cycle. H<sub>2</sub>O and C<sub>(s)</sub> selectivities were also similar at around 10%.

Subsequent to another step of *in situ* regeneration and reactivation, the catalyst exhibited similar performance as in the second cycle, but also with slight decrease in CH<sub>4</sub> and CO<sub>2</sub> conversions. The slight deactivation in this cycle can also be explained by catalyst sintering. CH<sub>4</sub> and CO<sub>2</sub> conversions were initially at 55 and 61% and decreased to 44 and 54% during the test. H<sub>2</sub> and CO selectivity were constant at 80%. Also, H<sub>2</sub>O and C<sub>(s)</sub> were kept around 10% during 30 h of test.

TEM images of the spent catalyst after the three cycles of DRM/regeneration confirms the catalyst deactivation by sintering. Fig. 7

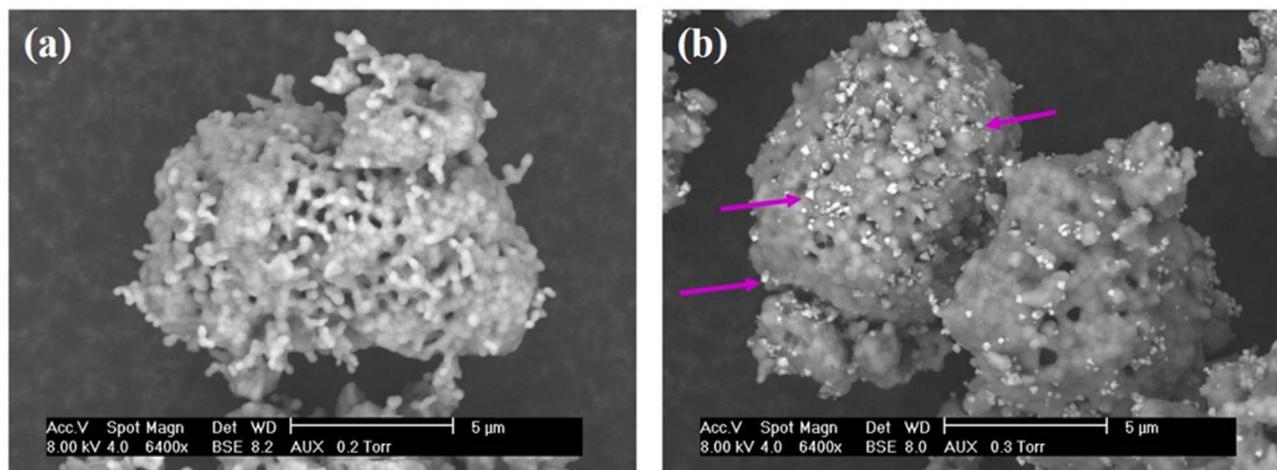


Fig. 3. SEM images of (a) Ca-HA1 support and (b) Ni/Ca-HA1\_S catalyst; → Ni particle.

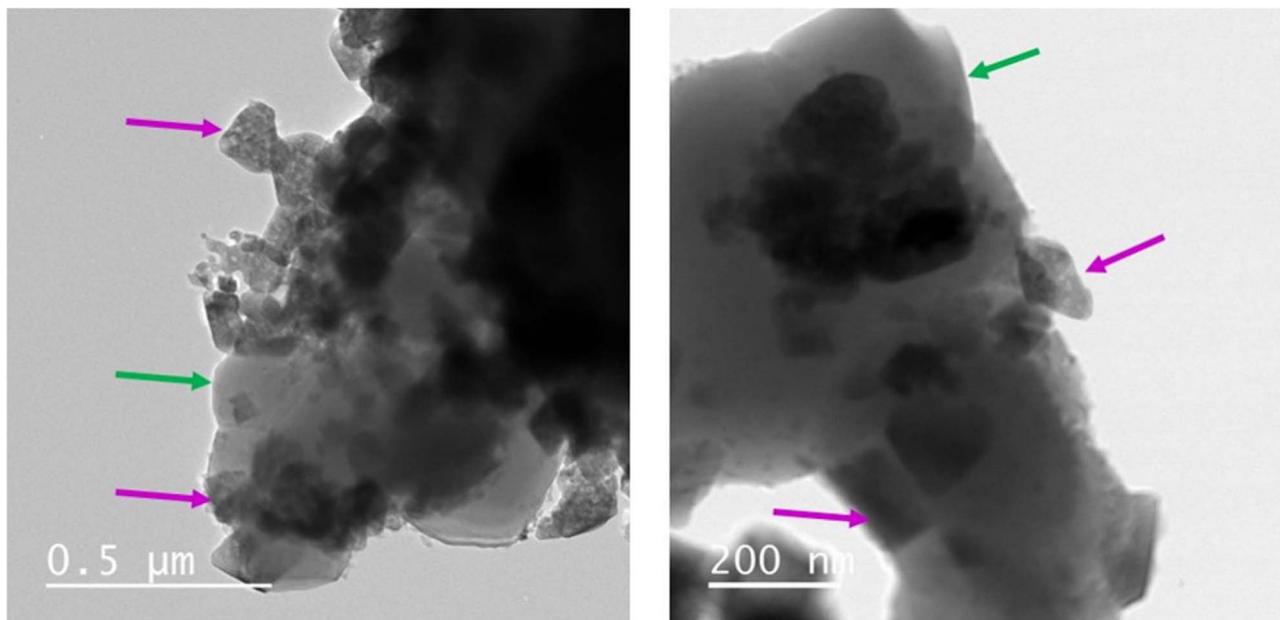


Fig. 4. TEM of Ni/Ca-HA1\_S fresh catalyst; → Ni particle, → hydroxyapatite.

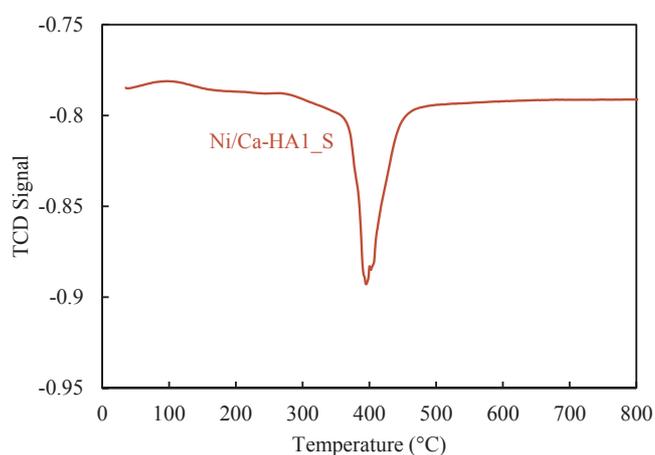


Fig. 5. TPR curve of the Ni/Ca-HA1\_S catalyst.

presents the TEM images of the spent catalyst after three cycles of DRM/Air regeneration.

Fig. 7a shows the formation of carbon deposit in the form of carbon nanofibers (CNFs) and core-shell. The formation of carbon was possible due to the relatively low metal-support interaction (Fig. 5) and to the presence of large nickel particles (Fig. 4). The CNFs play minor role on the catalyst deactivation because they mostly grow away from the catalyst surface and do not cover the active sites [42–44]. Also, they can push nickel particles from the supports and in some cases, they do not encapsulate them. In many cases, the nickel particles are on the tip of the CNFs and thus still available to the reaction [42,44–46]. On the other hand, the core-shell structure covers completely the active site of the catalyst and is hardly removed, leading to catalyst deactivation [43,47]. So, the small decrease in the performance of the catalyst between each cycle could be partially related to the formation of core-shell carbon.

Fig. 7b and c illustrates nickel particles over the spent catalyst after three cycles of DRM/Air regeneration. The nickel particles on the spent catalyst have a completely different shape and structure than the nickel particles on the fresh catalyst (Fig. 4). They have round shape, size about 10–50 nm and are not porous. The nickel particles suffered densification during the reaction, losing their surface and porosity,

which could also explain the small irreversible catalyst deactivation between cycles. However, it is worth noting that these nickel particles of round shape and small sizes (10–50 nm) are not poisoned by coke. In fact, it is widely accepted that the formation of coke on small nickel particles is not energetically favored [8]. Moreover, it is the metallic step edges that act as growth sites for the carbon growth [48,49]. So, despite the small loss of activity due the densification of the nickel particles, it might have prevented the deposition of coke over these particles and thus stabilizing the catalyst. This also suggests that coke deposition occurred mainly in the first hours of the reaction while the nickel particles still had large size (100–200 nm) and square shape.

### 3.2.2. Catalytic performance under DRM/CO<sub>2</sub>-regeneration cycles

Fig. 8 shows the evolution with time on stream (TOS) of the CH<sub>4</sub> and CO<sub>2</sub> conversions as well as of the H<sub>2</sub>, CO, H<sub>2</sub>O and C<sub>(s)</sub> selectivities for the Ni/Ca-HA1\_S catalyst under three successive cycles of DRM/CO<sub>2</sub> regeneration. The results obtained with DRM/CO<sub>2</sub> regeneration cycles are very similar to those obtained with the DRM/Air regeneration cycles.

In the first cycle (blue dots), the Ni/Ca-HA1\_S catalyst showed initial CH<sub>4</sub> and CO<sub>2</sub> conversion around 70 and 76%, respectively and then decreased to 46% and 57%, respectively during 30 h of TOS. As for the previous results, this deactivation could be related to carbon deposition and/or catalyst sintering. H<sub>2</sub> and CO selectivity were kept constant around 90% during the test. Also, H<sub>2</sub>O and C<sub>(s)</sub> were stable around 10% during the test.

Subsequent to an *in situ* regeneration under 21%CO<sub>2</sub>/N<sub>2</sub> flow and reactivation under 4%H<sub>2</sub>/N<sub>2</sub>, a small decrease in the CH<sub>4</sub> and CO<sub>2</sub> was observed compared to the first cycle, indicating the presence of irreversible catalytic deactivation. Although, high syngas yield was obtained. H<sub>2</sub> and CO selectivities were stable and around 90% during the test. H<sub>2</sub>O and C<sub>(s)</sub> were also stable around 10% during the test.

The third cycle of DRM/CO<sub>2</sub> regeneration (green dots) showed similar results to the second cycle (red dots), but a small decrease in the initial CH<sub>4</sub> and CO<sub>2</sub> conversions was also observed. The slight deactivation in this cycle could also be explained by catalyst sintering. CH<sub>4</sub> and CO<sub>2</sub> conversions decreased from around 50 and 60% to 41 and 52%. However, as for the previous cycles, high H<sub>2</sub> and CO selectivities were obtained. H<sub>2</sub> and CO selectivities were constant at around 80% during 30 h of test. Consequently, low selectivity to byproducts was obtained. H<sub>2</sub>O and C<sub>(s)</sub> were constant at 10% during the test.

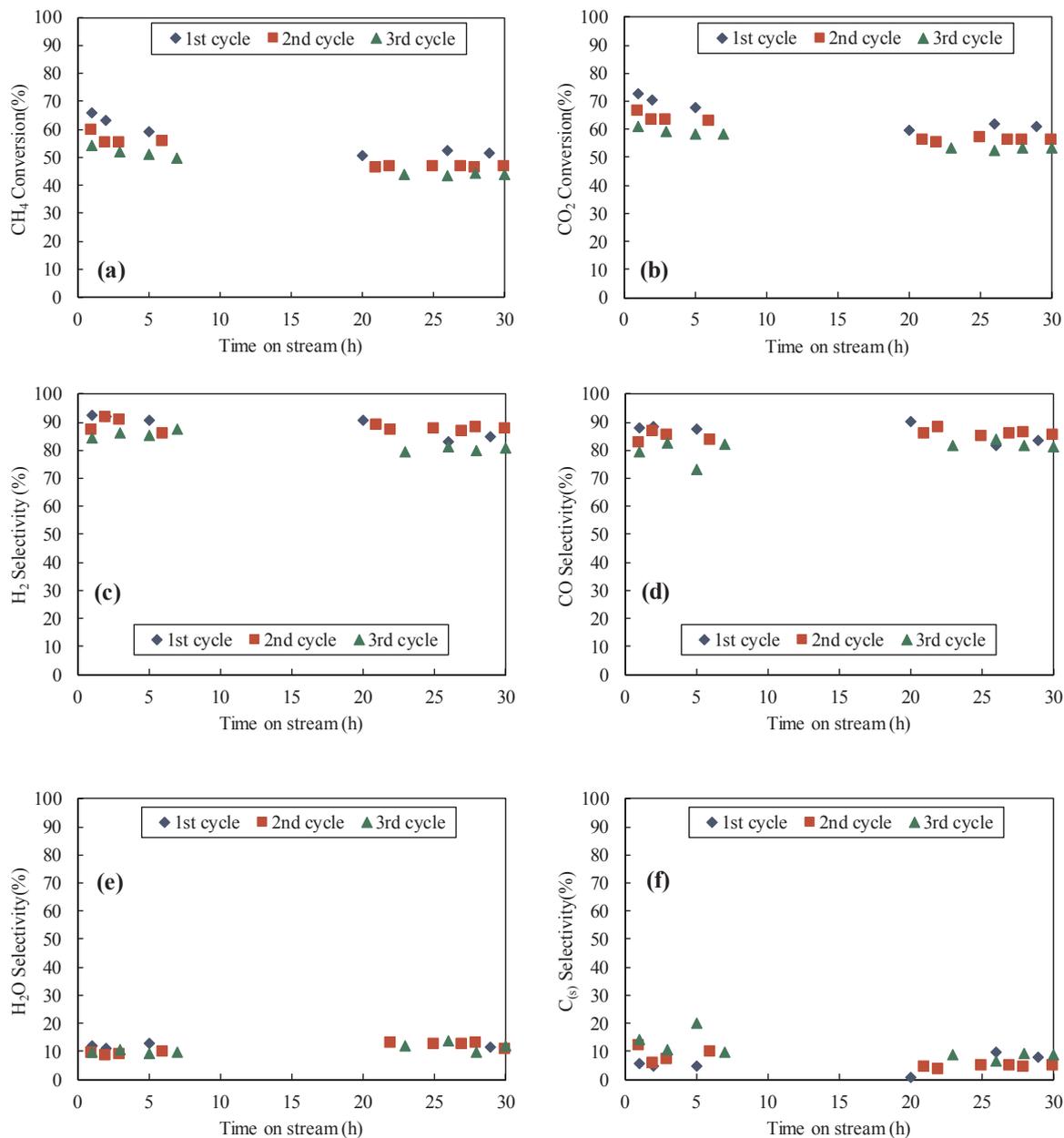


Fig. 6. Catalytic performance of Ni/Ca-HA1\_S catalyst under 3 cycles of DRM/Air-regeneration. Reaction conditions:  $T=700\text{ }^{\circ}\text{C}$ ,  $\text{WHSV} = 15882\text{ mL h}^{-1}\text{ g}_{\text{cat}}^{-1}$ ,  $\text{CH}_4/\text{CO}_2 = 1$ ,  $\text{TOS}=30\text{ h}$ . Regeneration conditions:  $1\text{h}30$  at  $700\text{ }^{\circ}\text{C}$  with air flow.

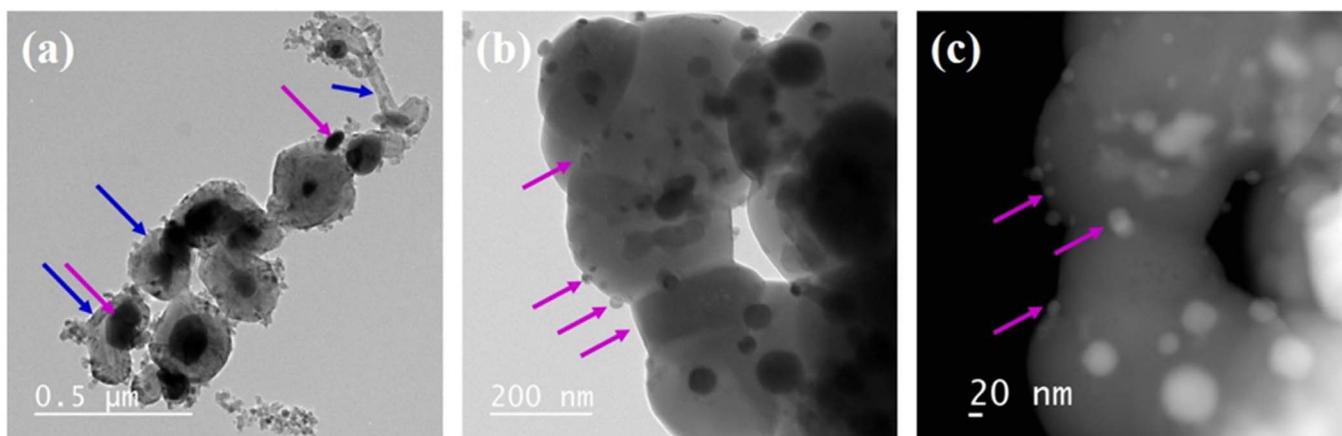
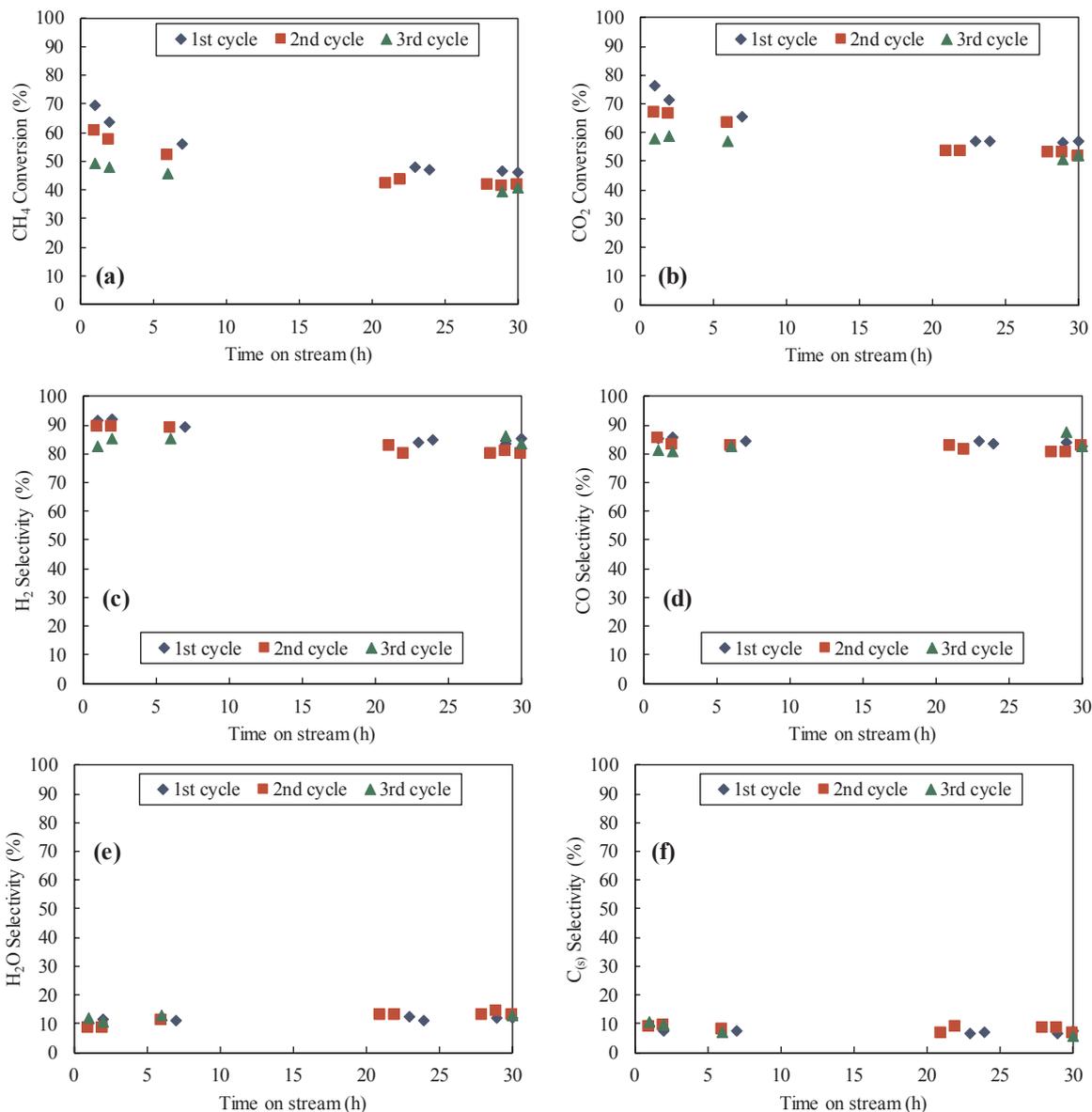


Fig. 7. TEM of Ni/Ca-HA1\_S spent catalyst after three cycles of DRM/Air regeneration;  $\rightarrow$  Ni particle,  $\rightarrow$  carbon.



**Fig. 8.** Catalytic performance of Ni/Ca-HA1\_S catalyst under 3 cycles of DRM/CO<sub>2</sub>-regeneration. Reaction conditions: T=700 °C, WHSV = 15882 mL h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>, CH<sub>4</sub>/CO<sub>2</sub> = 1, TOS=30 h. Regeneration conditions: 1h30 at 700 °C with 21%CO<sub>2</sub>/N<sub>2</sub> flow.

Fig. 9 presents the TEM images of the spent catalyst after three cycles of DRM/CO<sub>2</sub> regeneration.

Fig. 9a shows the presence of carbon deposit under CNFs and core-shell forms. These were already observed for the Ni/Ca-HA1\_S catalyst after 3 cycles of DRM/Air regeneration. The irreversible deactivation of this catalyst between the cycles was related to the formation of the core-shell carbon, which is hardly removed. Moreover, this catalyst also presented non-porous nickel particles with round shape and with size around 10–50 nm (Fig. 9b), indicating the occurrence of densification during the reaction. As previously explained, the densification of nickel particles provoked irreversible deactivation, which led to a small decrease in the performance of the catalyst. However, it also improved the stability of the catalyst since the formation of small nickel particles prevented the growth of coke.

Fig. 10 presents a summary of the results, comparing the values of CH<sub>4</sub> conversion and H<sub>2</sub> selectivity between regeneration under air and under CO<sub>2</sub>. The “fresh” and “spent” values correspond to the performance of the catalyst at the beginning and at the end of the first cycle, respectively. The values of “Regenerated (2nd cycle)” and “Regenerated (3rd cycle)” correspond to the values of performance at the beginning of

2nd and 3rd cycles after the regeneration step, respectively.

The results obtained with air regeneration are quite similar than those obtained with CO<sub>2</sub>/N<sub>2</sub> regeneration. The catalyst after regeneration steps with both atmospheres always showed higher CH<sub>4</sub> conversion than the spent catalyst (red column). This indicates that both atmospheres used could successfully regenerate the catalyst surface by eliminating the carbon deposit.

As previously presented, the values of CH<sub>4</sub> conversion after the regeneration steps are slightly lower than the CH<sub>4</sub> conversion values of the fresh catalyst (dark blue column) due to irreversible deactivation provoked by core-shell carbon formation and nickel particles densification. Nevertheless, the values of H<sub>2</sub> selectivity after regeneration steps under air and CO<sub>2</sub> were relatively stable and comparable to the H<sub>2</sub> selectivity of the fresh catalyst. This suggests that the occurrence of irreversible deactivation did not affect the selectivity of the catalyst to syngas.

These results showed that the Ni/Ca-HA1\_S catalyst can be easily regenerated under different atmospheres. An optimization of the regeneration step including changing the temperature and the duration of the regeneration are still needed to remove the core-shell carbon of the

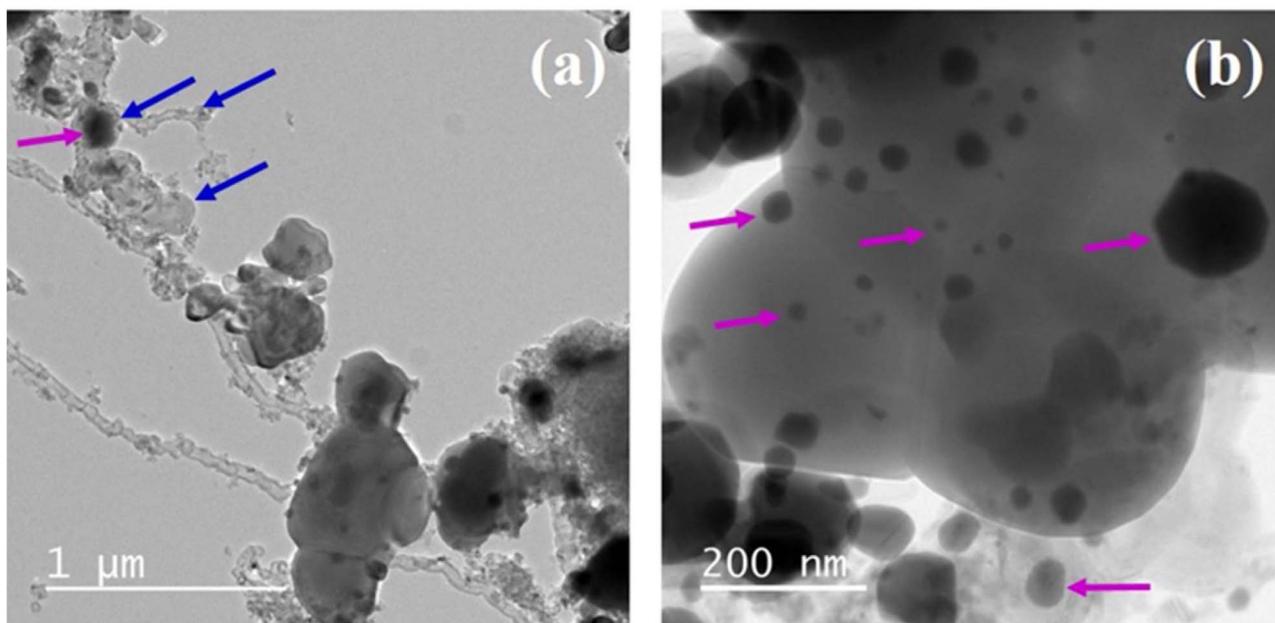


Fig. 9. TEM of Ni/Ca-HA1\_S spent catalyst after three cycles of DRM/CO<sub>2</sub> regeneration; → Ni particle, → carbon.

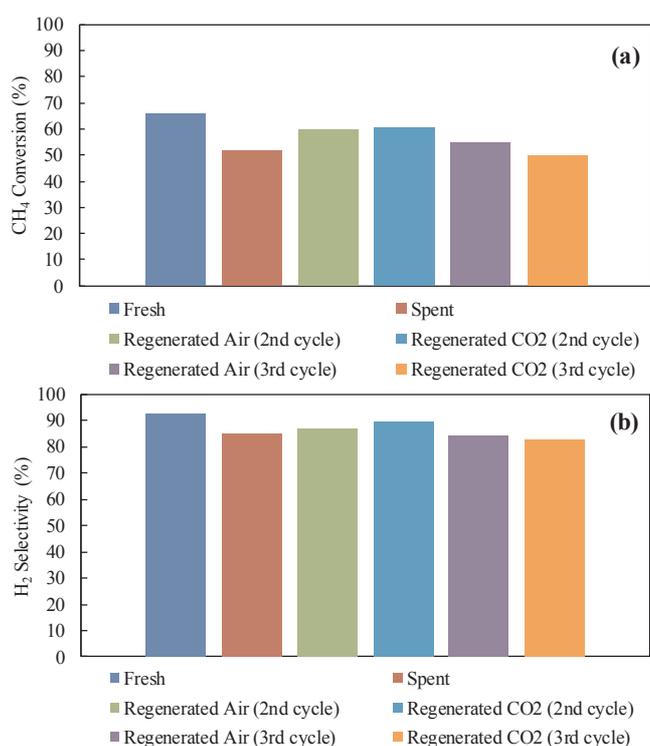


Fig. 10. Comparison between Air and CO<sub>2</sub> regeneration: (a) CH<sub>4</sub> conversion, (b) H<sub>2</sub> selectivity.

catalyst surface and obtain higher reactants' conversion.

#### 4. Conclusions

The regeneration of a hydroxyapatite-based catalyst (Ni/Ca-HA1\_S) was investigated during three successive cycles of DRM/regeneration. The *in situ* regeneration was carried out at 700 °C for 1h30 after a cycle of DRM at 700 °C for 30 h. The capacity of regeneration of the catalyst was tested under two different atmospheres: air and 21%CO<sub>2</sub>/N<sub>2</sub>. The catalyst presented good reproducibility between cycles for both atmospheres tested and only a small deactivation between cycles was

observed. The irreversible deactivation between cycles was provoked by the formation of core-shell carbon and by densification of the nickel particles during the reaction. However, after densification the nickel particles had round shape and small size (10–50 nm), which helped to prevent further carbon deposition. Despite the small loss in the reactants' conversion, the syngas selectivity was constant between cycles, which indicated that the deactivation of the catalyst did not affect its selectivity. These results showed the Ni/Ca-HA1\_S catalyst could be easily *in situ* regenerated under different atmospheres and make it competitive for dry reforming of methane. Further tests are needed to optimize the regeneration step and eliminate the core-shell carbon deposits.

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