

CO₂-SR Cyclic Technology: CO₂ Storage and *in situ* Regeneration with CH₄ over a new dual function NiBa unsupported catalyst.

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Highlights

- CO₂-SR Technology for Carbon capture and Hydrogen production
- NiBa catalyst is active in a cyclic process of CO₂-storage and CH₄ regeneration
- DRM and CH₄ decomposition are the main reactions in the regeneration step
- CO₂ and CH₄. Greenhouse Gases Capture and combined Utilization

Abstract

A Ni-Ba unsupported catalyst has been developed to be used as a dual function material (DFM) for a new CO₂ storage and in-situ regeneration (CO₂-SR technology), consisting in a CO₂ storage step followed by a CH₄ regeneration phase, working in alternating, cyclic and isothermal regime. The heterometallic mixed-oxide catalyst -NiO.BaO- used in this technology was prepared by an ultrasonic assisted coprecipitation using 1:1 atomic ratio (Ni:Ba) and colloidal silica as an agent promoting surface area and improving mechanical properties. The solid obtained maintains the *fcc*-structure at higher temperatures, demonstrates high reducibility as a bulky catalyst and presents a connected and balanced strong basic sites and CH₄ activation centres. It showed a CO₂-storage net capacity of 0.232 mmolCO₂·g⁻¹ and a CO₂ and CH₄ removal rate of 13.97% and 11.04% respectively, with a remarkable selectivity to hydrogen as an enriched-synthesis gas (H₂+CO) stream at 600 °C.

Keywords

CO₂-SR Technology; NiBa unsupported catalyst, Dual Function Material, CO₂-Storage, CH₄-Regeneration, syngas production.

1. Introduction

A new high record level of heat-trapping greenhouse gases (GHG) in the atmosphere has been reached. According to the latest bulletin about GHG issued by the World Meteorological Organization (WMO), carbon dioxide concentration in the atmosphere reached a new high level in 2019 of 413 ppm or 147% with respect to pre-industrial level in 1750 [1]. In fact, it is currently predicted that global warming is increasing the temperature 0.2 °C per decade mainly due to GHG emissions and it is also estimated that global warming is likely to reach 1.5 °C between 2030 and 2050 if the temperature continues to increase at this rate [2]. Therefore, in this scenario is necessary to mitigate CO₂ emissions, as the greatest GHG in the atmosphere, by development, reuse or revalorization technologies [3].

The most promising strategies are CO₂ sequestration are Carbon Capture and Storage or Utilization (CCS or CCU), besides, other techniques such as, absorption-desorption by aqueous solutions, use of membranes, adsorption and mineralization systems [4] that permit its reutilization and valorization [5,6], giving not only environmental but also economic benefits. An efficient adsorption process requires materials with an adequate specific area, a suitable porous structure, as well as some chemical properties such as high affinity to the adsorbate. Different functionalized materials for CO₂ sequestration have been developed, operating in a wide range of temperature and conditions. The use of alkali ceramics and alkali-earth oxides [7–12] for CO₂ capture at high temperatures (>500 °C) presents advantages to be used in CCU techniques [13–15].

Dual function materials (DFMs) as an alternative to CCS processes were reported by *Farrauto's* group [16]. These materials are capable of both capturing CO₂ and catalyzing its conversion to more valuable chemicals. Specifically, capture and conversion at the exhaust of combustion sources (e.g. flue gas at power plants) is an attractive option for CO₂ valorization. The concept lies in utilizing a high surface area supported solid adsorbent for the capture step in contact with a catalyst which utilizes renewable hydrogen

for production of synthetic natural gas (methane-CH₄) in an isothermal cyclic process [17]. DFMs contain an alkali-metal or alkaline-earth metal (such as Na₂CO₃, K₂CO₃ and CaO) that absorb CO₂ and a noble metal (Ru and Ni) to promote the methanation reaction. Several studies in the literature use DFMs to achieve CO₂ storage and hydrogenation to CH₄ [16,18–21]. The approach of producing chemicals and fuels directly from industrial flue gases over a DFM has been previously applied to the syngas production by a tri-reforming of methane process, a combination of CO₂ reforming, steam reforming and partial oxidation of methane with nickel supported catalysts [22,23].

The strategy of CO₂ revalorization into syngas using CH₄, as the second most harmful gas in the atmosphere, via dry reforming of methane (DRM) could be another alternative for the simultaneous reduction of two GHG emission [24], using a DFM for a cyclic-alternated technology to achieve CO₂ storage at high temperatures and reaction with a CH₄ stream. DRM is a very endothermic reaction, favored at high operating temperatures, in the range of 600-1000 °C and low pressures.



Although Eq.1 is the predominant reaction, several and parallel reactions may occur as was reported by *Nikoo et al.* [25]. The main drawback of implementing this process at an industrial scale is the need to reach high operating temperatures, which makes it necessary to use a catalyst such as a nickel supported in alumina, which is the most used [26]. The activity of these heterogeneous catalysts has been studied based on the influence of various parameters such as active metals [27–29], supports [30] and promoters [31,32]. In this case, the design of a DRM catalyst with an alkaline-earth oxide as promoter can provide the capacity to CO₂ capture and storage at high temperatures and at the same time favors its catalytic regeneration allowing the elimination of kinetic limitations of process and working on a type of chemical loop.

The aim of the present work is to develop an efficient Ni-based Ba-modified catalyst, as a dual function material, with adequate physicochemical properties and test its performance in the CO₂ Storage-Regeneration Technology; operating in transient, isothermal and cyclic regime. This technology consists on CO₂-capture by a storage step and a regeneration cycle of catalyst by the injection of CH₄ (or biogas) to yield a hydrogen-enriched gas stream.

2. Experimental

2.1. Catalyst preparation

A novel unsupported metal-alkaline earth metal catalyst was prepared employing an atomic ratio Ni/Ba=1/1 by coprecipitation with ammonia (30 vol.%) using nickel nitrate and barium nitrate as precursors (Panreac Applichem). 3% in atomic mass respect to Ni+Ba of colloidal silica (LUDOX HS-40, Aldrich Chemistry, 40 wt.% SiO₂) was added to the mixture. The solution of the precursors and colloidal silica was kept under stirring overnight at 30 °C. Then, it was twice sonicated at room temperature for 5 s before ammonia was dropwise added up to pH = 9. The equipment used consisted of Ultrasonic Processor UIP1000hd (Hielscher) with unchangeable frequency of 20 kHz using a titanium sonotrode. The ultrasonic power intensity was 300 W·cm⁻². After ultracentrifugation, the gel was washed with distilled water and dried for 24 h at 80 °C and finally calcinated at 800 °C (ramp of 5 °C·min⁻¹) in air for 4 h.

2.2. Physicochemical characterization

X-Ray Powder Diffraction data was recorded using an X'Pert Pro MPD diffractometer (PANanalytical) using a CuK α 1 radiation ($\lambda=1.5406$ Å) and a Ge(111) primary monochromator. Measurements were done from 10 to 70 ° (2 Θ) and average crystallite size was calculated by *Debye-Scherrer* equation.

BET Area (m²·g⁻¹) was determined using Brunauer-Emmet-Teller (BET) method and pore volume and pore size by Barret-Joyner-Halenda (BJH) methods in a Micromeritics ASAP 2020 Analyzer by adsorption-desorption of N₂ at 77 K in which solid was previously outgassed in vacuum (1·10⁻³ Pa) at 80 °C.

Raman spectra were collected in a DXR Raman Microscope (Thermo Scientific), working at 532 nm and 10 mW and with a Charge Couple Device (CCD) detector. Spectra were recorded in the 100-2000 cm⁻¹ Raman shift range with an accumulation time of 5 s.

CO₂ adsorption capacity of catalyst at high temperature was calculated using the experimental set up described below for the catalytic tests. The signal of CO₂ was monitored by a mass spectrometer (MS) and the value of CO₂ stored was calculated by subtraction of the numerical integrated responses for CO₂ fed and the CO₂ line registered during a rectangular pulse of 2,000 ppm of CO₂ according to Eq.2 at 600, 650 and 700 °C for reduced catalyst in H₂-atmosphere:

$$\frac{\text{CO}_2^{\text{stored}} (\text{mol}_{\text{CO}_2})}{g_{\text{cat}}} = \frac{A_{\text{CO}_2}^{\text{retained}} \cdot F}{g_{\text{cat}}} \quad \text{Eq.2}$$

where $A_{\text{CO}_2}^{\text{retained}}$ is the net adsorbed CO_2 and F represents the total fed volumetric gas flow.

CO_2 -Temperature-Programmed Desorption (CO_2 -TPD) was carried out in a flow system using $100 \text{ mL} \cdot \text{min}^{-1}$ of gas with 2,000 ppm of CO_2 and a temperature ranging from 60 to $800 \text{ }^\circ\text{C}$ with a ramp of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ in helium. The sample, 60 mg of catalyst, was placed in a quartz U-shaped reactor and, firstly, was pretreated for 1 h in helium and activated for 1h in a 2% H_2 balanced in He stream at $600 \text{ }^\circ\text{C}$. After that, CO_2 was adsorbed at 60°C , a He purge was performed and finally the temperature was increased. The gas-off was analysed with the QMS 200 mass spectrometer (Pfeiffer Vacuum Prisma™).

H_2 -Temperature-Programmed Reduction (H_2 -TPR) was performed using a flow of $50 \text{ mL} \cdot \text{min}^{-1}$ with 4% H_2 (in Ar) and a temperature ranging from $50 \text{ }^\circ\text{C}$ to $800 \text{ }^\circ\text{C}$ with a ramp rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$. 60 mg of catalyst was placed in a quartz U-shaped reactor. The sample was pre-treated in air for 60 min at $600 \text{ }^\circ\text{C}$. A molecular sieve was placed after the reactor to remove water, and a thermal conductivity detector was used to analyse the outlet gas in a Hewlett Packard HP 6890 gas chromatograph equipped with a TCD detector.

2.3. CO_2 -performance experiments

To test the CO_2 -SR Catalytic Technology behavior: CO_2 storage and regeneration alternated cyclic steps were performed using a quartz U-shaped fixed-bed reactor at atmospheric pressure connected to a QMS 200 mass spectrometer (Pfeiffer Vacuum Prism™). In each experiment, 60 mg of NiBa catalyst have been used, maintaining a constant total flow of inlet gas of $100 \text{ mL} \cdot \text{min}^{-1}$ at GHSV of $2.12 \cdot 10^4 \text{ h}^{-1}$. Previously, the catalyst was *in situ* conditioned in He up to the activation temperature ($600 \text{ }^\circ\text{C}$) and then reduced in a stream of H_2 (2% in He, $100 \text{ mL} \cdot \text{min}^{-1}$) for 1 h followed by a He purge. Alternated pulses of CO_2 and CH_4 diluted in He of 10 min and 10,000 ppm, each one, with an He purge, were performed at 600, 650 and $700 \text{ }^\circ\text{C}$. The following $m \cdot z^{-1}$ signals were registered: 2 (H_2), 4 (He), 12 (C), 14 (N), 16 (CH_4), 18 (H_2O), 28 (CO), 31 (MeOH), 32 (O_2), 40 (Ar) and 44 (CO_2) and in all cases Ar was used as a tracer, these signals were selected in order to avoid any influence between the compounds and were normalized and calibrated.

The percentage of CO₂ stored + converted was calculated according to Eq. 3 and the % of CH₄ converted according to Eq. 4.:

$$\%CO_2^{\text{sto+conv}} = \frac{\text{mol } CO_2^{\text{stored+converted}}}{\text{mol } CO_{2,\text{in}}} \cdot 100 \quad \text{Eq.3}$$

$$\%CH_4^{\text{conv}} = \frac{\text{mol } CH_4^{\text{converted}}}{\text{mol } CH_{4,\text{in}}} \cdot 100 \quad \text{Eq.4}$$

Where mol CO₂^{stored+converted} and mol CH₄^{converted} were obtained by subtraction of the numerical integration of the calibrated MS responses for CO_{2in} or CH_{4in} and the CO₂ or CH₄ line registered during storage and regeneration steps, extended almost for 10 alternating cycles, respectively. Whereas, the selectivity values of H₂ and CO, as main products, were calculated from the following equations:

$$S_{H_2} = \frac{\text{mol } H_2^{\text{produced}}}{\sum_{j=0}^P \text{mol product}_j} \cdot 100 \quad \text{Eq.5}$$

$$S_{CO} = \frac{\text{mol } CO^{\text{produced}}}{\sum_{j=0}^P \text{mol product}_j} \cdot 100 \quad \text{Eq.6}$$

3. Results and discussion

3.1. Characterization of catalyst

The textural properties of NiBa unsupported catalyst were measured. BET area was 112 m²·g⁻¹, exceptionally higher than those presented in the literature for similar non-supported materials [19,33], it presented mesoporous structure, small pore volume (0.18 cm³·g⁻¹) and a discrete pore size diameter of 64 Å. The incorporation of colloidal silica provides an improvement of textural properties to the catalyst.

Figure 1 shows the XRD patterns and the corresponding Raman spectra of NiBa catalyst calcined at 800 °C in air and after H₂-activation. For calcined NiBa catalyst, the most intense lines were detected at 43.5, 37.5 and 62.8° that correspond to the well-crystallized NiO_x (x=1-2) cubic phase (JCPDS 78-0643), with an average crystal size of 15 nm, estimated by *Debye Scherrer* equation. Additional peaks corresponding to Ba-containing species were not detected. A complete substitution of Ba in the crystalline NiO lattice can

be assumed, forming Ni(Ba)O_x-like species by the incorporation of Ba in Ni maintaining its cubic structure. Lattice parameters were obtained and it can be observed that $a=b=c=4.18 \text{ \AA}$ and cell volume is close to 73 \AA^3 ; due to NiO and BaO have *fcc*-structures with relatively close lattice parameters, 4.1946 and 3.970 \AA and Ni-O and Ba-O bond distances of 2.10 and 2.42 \AA , respectively. Only minor diffraction lines associated with barium carbonate (JCPDS 71-2394) and barium metasilicate species (JCPDS 26-1403) are distinguished, probably related to solid reactions between Ba and Si to form these stable and segregated species as a consequence of the high temperature of calcination.

After the activation in H₂ atmosphere (Fig.1.b) the XRD pattern is dominated by Ni-metallic species (JCPDS 04-0850) whose crystal size is maintained in 15 nm; with shorter length edges than Ni-Ba calcined since $a=b=c=3.53 \text{ \AA}$ and the reduction by almost half of cell-volume at 44 \AA^3 . No Ni-oxides associated signals were detected, although signals of barium carbonate and barium silicate were still present.

It is remarkable the complete reducibility of this nickel barium-substituted oxide, which maintains the cubic structure and does not compromise the solubility of barium since no apparent segregation was observed in the material after reduction. Ni-Ba oxidized catalyst XRD pattern agreed well with the peaks for the NiO standard, indicating a relative higher purity of the synthesized material. The method was reliable to reproduce NiBa non-supported calcined at high temperature catalyst with the same Ni-oxide structure. It should be noted that bimetallic non-supported calcined catalyst only exhibited NiO-peaks indicating a high solubility of BaO inside of NiO structure; besides, Ni-metal reflections peaks at 44 and 52° were not registered suggesting the formation of a mix-oxide Ni–Ba structure. The intensity of XRD signals reflected the crystallinity of the material and the width of the diffraction lines indicated very small size crystallites. The particle size estimated for pure NiO is close to the NiBa-oxide size, as was reported in the literature for NiO catalysts prepared using different techniques [34]; which is consistent with the measured BET-surface areas.

Regarding the Raman spectra, a relative weak broad non-defined band near 510 cm^{-1} and an intense mode close at 1050 cm^{-1} are the modes expected for pure NiO Raman spectra, the latter attributed to Ni-O stretching mode and lower shift-mode by formation of non-stoichiometric nickel oxide species. However, these signals are further modified when Ba is incorporated to NiO containing catalysts. This fact indicates that Ba interacts with NiO species, modifying both the 510 and 1100 cm^{-1} mode intensities due to Ba-interaction

with the NiO-structure at surface level mainly in supported catalysts or in Ba intercalation in NiO lattice for thin-films materials. XRD analysis is not sensitive enough to reveal different levels of oxides phases. So, in the Raman spectrum profile registered for Ni-Ba non-supported catalyst calcined at 800°C, an intense, wide and distorted signal is distinguished between 1250-950 cm^{-1} assigned to Ni-O stretching modes of $\text{Ni}^{+\delta}$ -oxidized species, in addition to the less-intense evident signals at 560 and 440 cm^{-1} , besides another signal at 511 cm^{-1} . The modes at 560 and 440 cm^{-1} could be associated with Ni-O vibrations in different Ni chemical environment, in a face-sharing chains of NiO_6 -octahedra and a square-planar coordination forming chains of edge-sharing NiO_4 -squares, and probably, partially distorted by the incorporation of BaO and the formation of a mixed species containing Ni^{2+} as $\text{NiO}\cdot\text{BaO}$ and Ni^{4+} as $\text{NiO}_2\cdot\text{BaO}$. The peripheral mode at 511 cm^{-1} can be also assigned to BaCO_3 [35] presence as was also detected in the XRD pattern.

Moreover, for H_2 -activated catalyst at 600°C for 2h in 2% H_2 -He atmosphere the Raman spectrum showed an unusual flat-profile, where the Ni-oxide associated modes almost completely disappeared and the mode detected at 511 cm^{-1} related to BaCO_3 species only remained. The loss of the Raman signal is not associated with an amorphization of the material since none intermetallic compound formation was found and the catalyst. However, the reduced Ni species must be linked to BaO species, resulting in a structurally isomorphic to Ni-metallic material and Ni-reduced species linked to BaO that gives a barium-oxide nickel reduced structure, which is non-Raman active.

H_2 -TPR profile of the pure NiO showed a quasi-symmetrical reduction profile between 300 and 500 °C, centered at 400 °C, which has been explained as one-step reduction of NiO to Ni ($\text{Ni}^{2+} \rightarrow \text{Ni}^0$) [36]. However, the H_2 -TPR profile registered for NiBa calcined catalyst is shown in Fig.2. Deconvolution of the reduction signal profile was conducted using Gaussian functions and it showed two evident reduction peaks between 400-750 °C, located at 565 and 676 °C. Additionally, a weak H_2 -consumption at 770 °C was detected and assigned to the decomposition-reduction of barium carbonate. The presence of different H_2 -consumption at higher temperatures than the registered for NiO, indicated that the Ni-cations species are necessarily and strongly stabilized by barium incorporation and the surrounding species provoke these shift-temperature associated to a multistep hydrogen consumption processes, separated 110 °C, meaning that different Ni-oxidized species are interacting with Ba-atoms.

As there was no modification of the NiO particle size by substitution with Ba²⁺ ions in the cubic structure, the shift in the reduction temperature and H₂-consumption profile could be due to the presence of different Ni oxidation states linked to Ba-O ions. At 565 °C the maximum could be associated with Ni⁴⁺ reduction to Ni²⁺ that forms part of NiO₂.BaO particles (NiO₃Ba) [36] and the maximum located at 676 °C should be associated with a second reduction step of Ni²⁺ species in the NiO.BaO (NiO₂Ba) particles to finally form stable Ni.BaO particles. Two different temperature intervals are found because the material presents different bulk-mixed-oxide structures. The lower reduction temperature would result in a quasi-complete conversion to form a complex polycrystalline NiO-Ni.BaO porous structure and a full reduction to Ni.BaO would be achieved during reduction at higher temperatures.

CO₂-TPD curve of Ni-Ba catalyst was performed after reduction to understand the stability of CO₂ adsorbed and stored on the surface and the result is showed in Figure 2. The profile presents an unique sharp signal between 550 and 750 °C with a T_{max} at 650 °C and no signals at low or moderate temperatures which should be related to weak or moderate basic sites were registered. This high-temperature peak is associated with CO₂ desorption from strong basic sites, which correspond to BaO interacting to Ni species. Due to the fact that the desorption temperature is very high and the temperature range in which desorption occurs is very narrow, CO₂, in dry conditions, is retained mainly as carbonate (CO₃²⁻) indicating that more stable polydentate carbonates species are the main species retained by material. It is important to note that the CO signal evolves increasing when the maximum of CO₂ signal is reached, and this signal drops sharply by reaction of part of the CO₂ retained on the reduced NiBa surface. Calculated CO₂ stored was of 87.61% that corresponds to 18.22 mmol CO₂·g_{cat}⁻¹. This value must keep in mind that the CO₂ is stored on the outer surface as bulk of the oxide favored by a single distribution of strong basic oxide sites and by a more advantageous for CO₂-capture and storage. CO₂-storage net capacity was calculated by numerical integration and the values were reported in Table 2. Taking into account that part of CO₂ is retained and partially desorbed (36 %) during the He purge step, such that the difference between CO₂ fed (CO₂ⁱⁿ area) and [CO₂^{adsorbed} - CO₂^{desorbed}] determines the net retention capacity. It was found that NiBa catalyst has a dynamic CO₂ adsorption capacity of 0.232 mmolCO₂·g_{cat}⁻¹, equivalent to 0.01 gCO₂·g_{cat}⁻¹, at 600 °C. This value compared with bibliographic data of other adsorbents with CO₂ retention capacity such as hydrotalcites [37], zeolite 13X [38] and

alkaline metal oxides as a CaO and K₂CO₃ [39] at high temperatures is not far from those reported, regardless of the overall retention capacity mechanism. So, the CO₂ retention capacity value increases up to 0.370 mmolCO₂·g_{cat}⁻¹ at 650 °C and drops to 0.15 mmolCO₂·g_{cat}⁻¹ at 700 °C; trend associated with gas-solid reaction connected to the CO₂ decomposition equilibrium. This Ni-Ba catalyst peculiarity facilitates the dual function material capacity.

3.2. Catalytic Activity

The isothermal alternated cyclic performance of Ni-Ba catalyst in the CO₂ storage and regeneration process was evaluated, feeding CO₂-He and CH₄-He pulses (10,000 ppm each one and GHSV=21,220 h⁻¹) with an intermediate purge of He, using Ar as a tracer at 600, 650, and 700 °C as three different temperatures were used at ordinary pressure. The catalyst was previously reduced *in situ* at 600 °C under hydrogen atmosphere. In Figure 3, the concentration profiles of CO₂, CH₄, CO, H₂ and Ar at the reactor outlet at 280 minutes (7 cycles) are represented (Fig.3a). The steady-state is reached after the third operation cycle and the initial disturbance of the signals at the beginning of each cycle is due to the valve-shift. During the CO₂-storage step, for this feed, the saturation is reached within 3 minutes. In the regeneration step using methane (as a reducing and regenerating agent) both, CO₂ desorbed and H₂ formed are detected, although CO is also detected in less extension. In the next cycle during the CO₂-storage step an increased formation of CO was also evidenced. In Fig.3b, a magnification of the first and second cycles of operation is displayed. As can be seen, in the first cycle and during the CO₂-acumulation period, CO₂ signal presents a shorter breakthrough time in the saturation curve. Once the CO₂ storage-step was finished the reactor was purged with He and the CO₂ desorption mass-signal progressively decreased until it reaches zero. For the same cycle, the regeneration period starts by feeding 10,000 ppm of CH₄ and contemporaneously, joint to CO₂ desorption and with a delay time of 2.5 seconds, H₂ and CO appeared as main products. For a cycle (after steady state was reached), CO₂-stored and converted during the storage period, CH₄ conversion and CO and H₂ selectivity values calculated for the catalyst regeneration-step are showed in Table 1. At 600 °C, CO₂ overall retention as average conversion calculated for the storage-step was 13.97 %, being CO the unique product detected. During the regeneration-step, CH₄ conversion value was 11.04 %, with

a H₂/CO selectivity ratio close to 5.6, which is a hydrogen-selectivity higher than was expected, taking into consideration dry methane reforming equilibrium stoichiometry. This deviation has been attributed to the contribution of methane decomposition reaction. When the operation temperature was increased to 650 °C, both, net CO₂ storage capacity and CH₄ conversion values were higher than those calculated at 600 °C. The CO₂-stored value reached 0.37 mmol CO₂·g_{cat}⁻¹, almost 60 % higher compared to the lowest temperature tested. A significant increase in H₂/CO selectivity ratio up to a value of 11.7 was observed in parallel with the methane conversion increase to 16 % (>45%). These facts are directly related to the temperature-trend; so higher temperatures favor methane decomposition reaction and in turn a decrease in the production of CO by DRM. At 700 °C, the highest operation temperature tested, CH₄-conversion was 18.57 % and hydrogen selectivity was 95.31%. Nevertheless, net CO₂ storage capacity presented an opposite trend, an increase of the temperature provoked a decrease in the capacity of retention of CO₂ of 0.13 mmolCO₂·g_{cat}⁻¹ and, consequently the CO-selectivity was reduced up to halfway with respect to 600 °C.

Taking into account the experimental data and the product distribution registered, it is possible to argue that two key-processes are involved in cyclic and alternated technology, over Ni-Ba heterometallic-centers as DFM: i) CO₂ storage and accumulation as carbonates (CO₃-species) on stronger Ba-basis sites and, ii) CH₄ conversion on Ni-reduced mixed-centers, involving the carbonated centers which is the rate determining step, to produce H₂+CO by dry reforming of methane and the continuous regeneration of metal and basic sites.

Besides, CO₂-storage, involving heterometallic mixed-centers, and the production of CO and H₂ can be explained taking into account four different reactions, depending on the phase in the cycle and are described by the 7-10 equations: CO₂ activated decomposition [Eq.7], methane dry reforming DRM [Eq.8], CO₂-carbon gasification [Eq.9] and the internal reverse water-gas shift, RWGS as [Eq.10].





Eq.11

So, during CO₂ storage-phase, two activated processes can take place contemporaneously: the adsorption-retention of CO₂ on the catalyst and the reaction to yield CO, which also provides O* able to reoxidize Ni-reduced centers in Ni.BaO, according to the Eq.7. Additionally, CO₂(g) can also react with the C(s) originated from methane cracking reaction during the earlier CH₄ pulses used in the regeneration phase, yielding CO(g) by reverse Boudouard reaction [Eq.9] favored at higher temperatures [40], and also favor the catalyst regeneration by removal of deposited carbon, eventually. It is import to note that an additional *via* for the formation of CO and water was registered during the storage phase of each subsequent cycle, and should be associated with the RWGS parallel reaction contribution; through a H₂-enriched surface from the previous CH₄-regeneration step [Eq. 10]. *Osaki et al.* [41] reported, at temperatures close to 700 °C, a similar trend over Ni/Al₂O₃ catalysts, as was also evidenced for this non-supported NiBa catalyst.

During the reduction-phase using CH₄ as CO₂-regeneration agent, H₂, CO and CO₂ were detected and the major catalyzed reactions were methane dry reforming [Eq.8] and methane decomposition contribution as co-side reaction [Eq.11], promoted by the presence of Ni reduced species [42–45]. Estimated H₂/CO ratios are justified by the extension of both reactions that depends on the operation temperature as can be extracted from the experimental data. At the catalyst level, the reduction of Ni-oxidized centers also occurs, regenerating the catalyst and closing the chemical loop.

To evaluate the long-term behavior under steady state conditions with isothermal regime for NiBa, the number of cycles were extended up to 16 hours at 600 °C in the same feed conditions. The overall data registered concerning to CO₂ and CH₄ conversion and H₂/CO ratio values for alternating cyclic extra-time (8 + 8 hours with intermediate He flow overnight) as a function of the reaction time are displayed in Figure 4. As can be observed there is an initial significant decrease during the first six-cycles and then a stabilization of CO₂ and CH₄ conversion values, close to 4-5 % for both, occurs after four-hours; while the H₂/CO ratios seems to increase with a linear tendency. The H₂/CO ratio reaches a value greater than 50 after 16 hours of operation. These facts seem to be connected since the values of CO₂^{sto+conv} and CH₄^{conv} conversion data remain almost constant, because the

predominant reaction at high temperatures is dry reforming of methane (DRM). The increase of the operation time provokes the overlaps of methane-decomposition reaction causing deposition and deactivation by carbon. However, the contribution reaction of gasification of the carbon deposited onto catalyst by CO₂, seems to balance the increasing H₂/CO ratio maintaining the *quasi*-lineal trend.

Carbon deposition on the catalyst produces a considerable deactivation issue by its accumulation during regeneration-phase with methane. So, the formation and the nature of the carbon deposits was investigated by Raman, after each CO₂ storage and regeneration for two consecutive cycles. The data are provided in Figure 5. During the first CO₂-storage-phase pulse, no significant Raman modes were observed, except for a broad and weak signal at 1050 cm⁻¹, evident in the three spectra that is associated with the presence of polycrystalline NiO-Ni₃BaO non-fully reduced species. In the same cycle and during methane regeneration pulse, two Raman signals were evident, related to ordered graphitic G-band at 1574 cm⁻¹ and the disordered graphitic lattice D-band at 1324 cm⁻¹ [46,47]. In the second cycle and after the second CO₂ storage phase pulse, these bands were still observable, although the relative intensity was lower. This decrease in the signals intensities is due to the carbon content decreasing that approximately would represent a decrease in intensity of 45%. In the inset of the figure, the product distributions (H₂, CO, CO₂, and CH₄) registered by mass spectrometry are displayed for the different phases. It is noteworthy that in the regeneration phase for the first cycle, H₂ and CO formation is observed by the occurrence of dry-reforming and CH₄-decomposition reactions as reveal the H₂/CO ratio estimated. The C-balance indicates that part of the carbon contained in the methane molecule is deposited as solid, as suggested by the Raman record. So, in the second cycle and during the CO₂-storage phase, CO formation is registered, which is more probably to be formed via decomposition of the CO₃-retained species on catalysts rather than the reverse Boudouard reaction.

Even though the conversion seems to be relatively low, it has been verified with the durability test that NiBa catalyst performance is attributed to a sustained periodic cycle of carbon deposition and removal by gasification as well as the interaction between Ni and Ba, maintaining the performance to produce H₂-enriched streams and preventing the deactivation of the catalyst.

Based on the exposed results, the overall routes and a reaction network to describe the CO₂-SR transient technology for CO₂-capture and storage and its ulterior regeneration

using CH₄ (GHGs) have been considered, and a schematized picture is proposed in Figure 6. NiBa catalyst presents a high net CO₂ retention capacity at high temperatures, higher than other DFM reported in literature, and moderate activity in the conversion of CH₄, being able to work under alternating cycles CO₂-CH₄.

In this way, the novel high temperature CO₂-SR process for carbon capture-regeneration with syngas production has been proved, using a novel unsupported Ni-Ba catalyst, which is developed as a dual function material with a high CO₂-sorbent capacity and a regeneration-utilization by *in situ* methane reforming to produce H₂-enriched streams.

4. Conclusion

A non-supported Ni-Ba bifunctional catalyst with a high surface area and mechanical stability was developed and characterized. The heterometallic mixed oxide is presented as an excellent material to work isothermally in a transitory regime technology for storage and utilization of CO₂.

A novel concept, CO₂-SR technology, has been developed for carbon capture and hydrogen production using a DFM, which is a bimetallic oxide with a high-capacity as CO₂ sorbent and as improved methane conversion catalyst, for the production of H₂ enriched streams. The regeneration of the material and the conversion of stored-captured CO₂ by cycles, are carried out in a single reactor at the same temperature alternating the cyclic conditions. The catalyst works as CO₂-SR chemical loop system and uses two important GHG, such as CO₂ and CH₄.

The CO₂-storage capacity was 0.232 mmolCO₂·g_{cat}⁻¹. A CO₂ and CH₄ removal rate of 12.30 % and 15.4 % respectively, was obtained at 600 °C with a remarkable selectivity to hydrogen as an enriched-synthesis gas (H₂+CO) stream.

List of Tables and Figures

Table 1. CO₂ storage-capacity in the accumulation step above CO₂-He-Ar and CH₄ conversion and CO and H₂ selectivities during accumulation and regeneration steps at 600, 650 and 700°C above CH₄-He-Ar

Figure 1. XRD patterns and Raman spectra of NiBa catalyst. (a) calcined in air at 800°C; (b) activated at 600°C for 2h in 2% H₂-He atmosphere.

Figure 2. H₂-TPR and CO₂-TDP profiles of Ni-Ba catalyst calcined in air at 800 °C.

Figure 3. (a) CO₂, H₂, CH₄ and CO concentration profiles during alternating cycles of CO₂ and CH₄ regeneration over NiBa catalyst; (b) Magnification of first and second CO₂-He-CH₄ cycles at 600 °C.

Figure 4. CO₂^{sto+conv}, CH₄^{conv} conversion values and H₂/CO selectivity ratio recorded during 8 h catalytic runs at 600 °C under alternated cyclic conditions. Right-panel: Extra-time (8 more hours) under alternated cyclic conditions after He flow overnight at room temperature.

Figure 5. Raman spectra of NiBa catalyst after two consecutive cycles CO₂-He-CH₄ (10 minutes per pulse). (a) Initial CO₂ storage phase, (b) after saturation during regeneration phase using CH₄ pulse and (c) Second cycle after CO₂ pulse. Pulses of 10 minutes.

Figure 6. Scheme of proposed involved processes for the CO₂-SR technology over Ni-Ba unsupported catalyst.

Authorship contribution

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Declaration of Competing Interest

The authors declare that there are no conflicts of interest.

References

- [1] World Meteorological Organization, Global Atmosphere Watch, The State of Greenhouse Gases in the Atmosphere Based on Global Observations through 2018, WMO Greenh. Gas Bull. 15 (2019).
- [2] United Nations, Climate Agreement of Paris, (2015). <https://doi.org/10.1017/s0020782900004253>.
- [3] V. Masson-Delmotte, P. Zhai, H.-O. Pörtner, D. Roberts, J. Skea, P.R. Shukla, A. Pirani, W. Moufouma-Okia, C. Péan, R. Pidcock, S. Connors, J.B.R. Matthews, Y. Chen, X. Zhou, M.I. Gomis, E. Lonnoy, T. Maycock, M. Tignor, T. Waterfield, Global warming of 1.5°C. An IPCC Special Report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change, Cambridge University Press, Cambridge, 2018. <https://doi.org/10.1017/CBO9781107415324>.
- [4] A. Rafiee, K. Rajab Khalilpour, D. Milani, M. Panahi, Trends in CO₂ conversion and utilization: A review from process systems perspective, J. Environ. Chem. Eng. 6 (2018) 5771–5794. <https://doi.org/10.1016/j.jece.2018.08.065>.
- [5] H. Herzog, E. Drake, E. Adams, CO₂ Capture, Reuse, and Storage Technologies for Mitigating Global Climate Change, (1997).
- [6] F. Karimi, R. Khalilpour, Evolution of carbon capture and storage research: Trends of international collaborations and knowledge maps, Int. J. Greenh. Gas Control. 37 (2015) 362–376. <https://doi.org/10.1016/j.ijggc.2015.04.002>.
- [7] D. Peltzer, J. Mùnera, L. Cornaglia, M. Strumendo, Characterization of potassium doped Li₂ZrO₃ based CO₂ sorbents: Stability properties and CO₂ desorption kinetics, Chem. Eng. J. 336 (2018) 1–11. <https://doi.org/10.1016/j.cej.2017.10.177>.
- [8] H. Sun, C. Wu, B. Shen, X. Zhang, Y. Zhang, J. Huang, Progress in the

- development and application of CaO-based adsorbents for CO₂ capture—a review, *Mater. Today Sustain.* 1–2 (2018) 1–27. <https://doi.org/10.1016/j.mtsust.2018.08.001>.
- [9] C. Slostowski, S. Marre, P. Dagault, O. Babot, T. Toupance, C. Aymonier, CeO₂ nanopowders as solid sorbents for efficient CO₂ capture/release processes, *J. CO₂ Util.* 20 (2017) 52–58. <https://doi.org/10.1016/j.jcou.2017.03.023>.
- [10] E. Vera, J.F. Gómez-García, H. Pfeiffer, Enhanced CO₂ chemisorption at high temperatures via oxygen addition using (Fe, Cu or Ni)-containing sodium cobaltates as solid sorbents, *J. CO₂ Util.* 25 (2018) 147–157. <https://doi.org/10.1016/j.jcou.2018.03.019>.
- [11] A. MacKenzie, D.L. Granatstein, E.J. Anthony, J.C. Abanades, Economics of CO₂ Capture Using the Calcium Cycle with a Pressurized Fluidized Bed Combustor, *Energy & Fuels.* 21 (2007) 920–926. <https://doi.org/10.1021/ef0603378>.
- [12] J. Blamey, E.J. Anthony, J. Wang, P.S. Fennell, The calcium looping cycle for large-scale CO₂ capture, *Prog. Energy Combust. Sci.* 36 (2010) 260–279. <https://doi.org/10.1016/j.pecs.2009.10.001>.
- [13] L.C. Buelens, H. Poelman, C. Detavernier, G.B. Marin, V. V. Galvita, CO₂ sorption properties of Li₄SiO₄ with a Li₂ZrO₃ coating, *J. CO₂ Util.* 34 (2019) 688–699. <https://doi.org/10.1016/j.jcou.2019.08.022>.
- [14] Z. Abdelsadek, M. Sehalia, D. Halliche, V.M. Gonzalez-Delacruz, J.P. Holgado, K. Bachari, A. Caballero, O. Cherifi, In-situ hydrogasification/regeneration of NiAl-hydrotalcite derived catalyst in the reaction of CO₂ reforming of methane: A versatile approach to catalyst recycling, *J. CO₂ Util.* 14 (2016) 98–105. <https://doi.org/10.1016/j.jcou.2016.03.004>.
- [15] J.R. Fernández, J.C. Abanades, Optimized design and operation strategy of a Ca/Cu chemical looping process for hydrogen production, *Chem. Eng. Sci.*

- 166 (2017) 144–160. <https://doi.org/10.1016/j.ces.2017.03.039>.
- [16] M.S. Duyar, M.A.A. Treviño, R.J. Farrauto, Dual function materials for CO₂ capture and conversion using renewable H₂, *Appl. Catal. B Environ.* 168–169 (2015) 370–376. <https://doi.org/10.1016/j.apcatb.2014.12.025>.
- [17] M.A. Arellano-Treviño, Z. He, M.C. Libby, R.J. Farrauto, Catalysts and adsorbents for CO₂ capture and conversion with dual function materials: Limitations of Ni-containing DFMs for flue gas applications, *J. CO₂ Util.* 31 (2019) 143–151. <https://doi.org/10.1016/j.jcou.2019.03.009>.
- [18] M.S. Duyar, S. Wang, M.A. Arellano-Treviño, R.J. Farrauto, CO₂ utilization with a novel dual function material (DFM) for capture and catalytic conversion to synthetic natural gas: An update, *J. CO₂ Util.* 15 (2016) 65–71. <https://doi.org/10.1016/j.jcou.2016.05.003>.
- [19] H. Sun, J. Wang, J. Zhao, B. Shen, J. Shi, J. Huang, C. Wu, Dual functional catalytic materials of Ni over Ce-modified CaO sorbents for integrated CO₂ capture and conversion, *Appl. Catal. B Environ.* 244 (2019) 63–75. <https://doi.org/10.1016/j.apcatb.2018.11.040>.
- [20] A. Bermejo-López, B. Pereda-Ayo, J.A. González-Marcos, J.R. González-Velasco, Mechanism of the CO₂ storage and in situ hydrogenation to CH₄. Temperature and adsorbent loading effects over Ru-CaO/Al₂O₃ and Ru-Na₂CO₃/Al₂O₃ catalysts, *Appl. Catal. B Environ.* 256 (2019) 117845. <https://doi.org/10.1016/j.apcatb.2019.117845>.
- [21] H. Sun, Y. Zhang, S. Guan, J. Huang, C. Wu, Direct and highly selective conversion of captured CO₂ into methane through integrated carbon capture and utilization over dual functional materials, *J. CO₂ Util.* 38 (2020) 262–272. <https://doi.org/10.1016/j.jcou.2020.02.001>.
- [22] C. Song, W. Pan, Tri-reforming of methane: a novel concept for catalytic production of industrially useful synthesis gas with desired H₂/CO ratios, *Catal. Today.* 98 (2004) 463–484. <https://doi.org/10.1016/j.cattod.2004.09.054>.

- [23] M. Minutillo, A. Perna, A novel approach for treatment of CO₂ from fossil fired power plants, Part A: The integrated systems ITRPP, *Int. J. Hydrogen Energy*. 34 (2009) 4014–4020. <https://doi.org/10.1016/j.ijhydene.2009.02.069>.
- [24] N.A.K. Aramouni, J.G. Touma, B.A. Tarboush, J. Zeaiter, M.N. Ahmad, Catalyst design for dry reforming of methane: Analysis review, *Renew. Sustain. Energy Rev.* 82 (2018) 2570–2585. <https://doi.org/10.1016/j.rser.2017.09.076>.
- [25] M.K. Nikoo, N.A.S. Amin, Thermodynamic analysis of carbon dioxide reforming of methane in view of solid carbon formation, *Fuel Process. Technol.* 92 (2011) 678–691. <https://doi.org/10.1016/j.fuproc.2010.11.027>.
- [26] B. Abdullah, N.A. Abd Ghani, D.-V.N. Vo, Recent advances in dry reforming of methane over Ni-based catalysts, *J. Clean. Prod.* 162 (2017) 170–185. <https://doi.org/10.1016/j.jclepro.2017.05.176>.
- [27] M. García-Diéguez, I.S. Pieta, M.C. Herrera, M.A. Larrubia, L.J. Alemany, Nanostructured Pt- and Ni-based catalysts for CO₂-reforming of methane, *J. Catal.* 270 (2010) 136–145. <https://doi.org/10.1016/j.jcat.2009.12.010>.
- [28] M. García-Diéguez, I.S. Pieta, M.C. Herrera, M.A. Larrubia, L.J. Alemany, Improved Pt-Ni nanocatalysts for dry reforming of methane, *Appl. Catal. A Gen.* 377 (2010) 191–199. <https://doi.org/10.1016/j.apcata.2010.01.038>.
- [29] J.A.C. Dias, J.M. Assaf, Autoreduction of promoted Ni/ γ -Al₂O₃ during autothermal reforming of methane, *J. Power Sources.* 139 (2005) 176–181. <https://doi.org/10.1016/j.jpowsour.2004.07.029>.
- [30] Z. Rong-jun, X. Guo-fu, L. Ming-feng, W. Yu, N. Hong, L. Da-dong, Effect of support materials on the performance of Ni-based catalysts in methane dry reforming, *Fuel Process. Technol.* 43 (2015) 1359–1365. <https://doi.org/10.1016/j.fuproc.2018.12.018>.
- [31] M. Usman, W.M.A. Wan Daud, H.F. Abbas, Dry reforming of methane:

- Influence of process parameters—A review, *Renew. Sustain. Energy Rev.* 45 (2015) 710–744. <https://doi.org/10.1016/j.rser.2015.02.026>.
- [32] M. García-Diéguez, M.C. Herrera, I.S. Pieta, M.A. Larrubia, L.J. Alemany, NiBa catalysts for CO₂-reforming of methane, *Catal. Commun.* 11 (2010) 1133–1136. <https://doi.org/10.1016/j.catcom.2010.06.008>.
- [33] A. Löfberg, J. Guerrero-Caballero, T. Kane, A. Rubbens, L. Jalowiecki-Duhamel, Ni/CeO₂ based catalysts as oxygen vectors for the chemical looping dry reforming of methane for syngas production, *Appl. Catal. B Environ.* 212 (2017) 159–174. <https://doi.org/10.1016/j.apcatb.2017.04.048>.
- [34] S.K. Noukelag, H.E.A. Mohamed, B. Moussa, L.C. Razanamahandry, S.K.O. Ntwampe, C.J. Arendse, Structural and optical investigations of biosynthesized bunsenite NiO nanoparticles (NPs) via an aqueous extract of *Rosmarinus officinalis* (rosemary) leaves, *Mater. Today Proc.* (2020). <https://doi.org/10.1016/j.matpr.2020.03.314>.
- [35] R.E. Benner, J.R. Mitchell, R.W. Grow, Raman scattering as a diagnostic technique for cathode characterization, *IEEE Trans. Electron Devices.* 34 (1987) 1842–1847. <https://doi.org/10.1109/T-ED.1987.23163>.
- [36] E. Zacharaki, P. Beato, R.R. Tiruvalam, K.J. Andersson, H. Fjellvåg, A.O. Sjøstad, From Colloidal Monodisperse Nickel Nanoparticles to Well-Defined Ni/Al₂O₃ Model Catalysts, *Langmuir.* 33 (2017) 9836–9843. <https://doi.org/10.1021/acs.langmuir.7b02197>.
- [37] Z. Yong, Mata, A.E. Rodrigues, Adsorption of Carbon Dioxide onto Hydrotalcite-like Compounds (HTlcs) at High Temperatures, *Ind. Eng. Chem. Res.* 40 (2001) 204–209. <https://doi.org/10.1021/ie000238w>.
- [38] D. Ko, R. Siriwardane, L.T. Biegler, Optimization of a Pressure-Swing Adsorption Process Using Zeolite 13X for CO₂ Sequestration, *Ind. Eng. Chem. Res.* 42 (2003) 339–348. <https://doi.org/10.1021/ie0204540>.
- [39] L. Nie, Y. Mu, J. Jin, J. Chen, J. Mi, Recent developments and consideration

- issues in solid adsorbents for CO₂ capture from flue gas, *Chinese J. Chem. Eng.* 26 (2018) 2303–2317. <https://doi.org/10.1016/j.cjche.2018.07.012>.
- [40] K. Nagase, T. Shimodaira, M. Itoh, Y. Zheng, Kinetics and mechanisms of the reverse Boudouard reaction over metal carbonates in connection with the reactions of solid carbon with the metal carbonates, *Phys. Chem. Chem. Phys.* 1 (1999) 5659–5664. <https://doi.org/10.1039/a906687j>.
- [41] T. Osaki, T. Mori, Kinetics of the reverse-Boudouard reaction over supported nickel catalysts, *React. Kinet. Catal. Lett.* 89 (2006) 333–339. <https://doi.org/10.1007/s11144-006-0145-9>.
- [42] L. Dong, Y. Du, J. Li, H. Wang, Y. Yang, S. Li, Z. Tan, The effect of CH₄ decomposition temperature on the property of deposited carbon over Ni/SiO₂ catalyst, *Int. J. Hydrogen Energy.* 40 (2015) 9670–9676. <https://doi.org/10.1016/j.ijhydene.2015.06.005>.
- [43] L. Smoláková, M. Kout, L. Čapek, A. Rodriguez-Gomez, V.M. Gonzalez-Delacruz, L. Hromádka, A. Caballero, Nickel catalyst with outstanding activity in the DRM reaction prepared by high temperature calcination treatment, *Int. J. Hydrogen Energy.* 41 (2016) 8459–8469. <https://doi.org/10.1016/j.ijhydene.2016.03.161>.
- [44] Z. Li, B. Jiang, Z. Wang, S. Kawi, High carbon resistant Ni@Ni phyllosilicate@SiO₂ core shell hollow sphere catalysts for low temperature CH₄ dry reforming, *J. CO₂ Util.* 27 (2018) 238–246. <https://doi.org/10.1016/j.jcou.2018.07.017>.
- [45] F. Frusteri, G. Italiano, C. Espro, F. Arena, CH₄ decomposition on Ni and Co thin layer catalysts to produce H₂ for fuel cell, *Catal. Today.* 171 (2011) 60–66. <https://doi.org/10.1016/j.cattod.2011.03.016>.
- [46] Q. Ma, L. Guo, Y. Fang, H. Li, J. Zhang, T.-S. Zhao, G. Yang, Y. Yoneyama, N. Tsubaki, Combined methane dry reforming and methane partial oxidization for syngas production over high dispersion Ni based mesoporous catalyst, *Fuel Process. Technol.* 188 (2019) 98–104.

<https://doi.org/10.1016/j.fuproc.2019.02.013>.

- [47] S. Zhang, S. Muratsugu, N. Ishiguro, M. Tada, Ceria-Doped Ni/SBA-16 Catalysts for Dry Reforming of Methane, *ACS Catal.* 3 (2013) 1855–1864. <https://doi.org/10.1021/cs400159w>.