Catalytic performances of Ni–CaO–mayenite in CO2 sorption enhanced steam methane reforming

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Ni–CaO–mayenite (Ca12Al14O33) catalysts for the CO2 Sorption Enhanced Steam Methane Reforming (SE-SMR) have been developed using the microwave assisted self-combustion method of preparation. The sorption of CO2 by CaO shifts the steam reforming and the Water Gas Shift reaction (WGS) towards H2 production and favors the heat balance of the global reaction. The CO2 sorption has been studied on materials with different CaO/Ca12Al14O33 ratios and for different types of preparation. The specific surface area of materials, the temperature of Ni phases’ reducibility and CO2 sorption are all essential for material efficiency. The Ni–CA75MM catalyst was the most active and stable in methane steam reforming with CO2 sorption, even at an unusually low temperature (650 °C).

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1. Introduction

The research and development of new sources of “clean” energy which reduce the emission of greenhouse gases are necessary. Carbon dioxide emission (CO2) is a major contributor to global warming and one-third of those emissions come from fuel combustion for power generation [1].

Hydrogen is mainly obtained from syngas resulting from natural gas steam reforming (SMR). Syngas production by methane reforming is always accompanied by CO2 formation, and its capture by absorption on a solid oxide could be a convenient strategy to improve CH4 conversion and H2 selectivity and to concentrate CO2 for the eventual use as chemicals or as energy vectors. CaO is often chosen as the CO2 sorbent because of its high efficiency in carbonation and its easy regeneration by CaCO3 calcination. When CO2 sorption is desired, the presence of solid oxide requires the need to work at relatively low temperatures (600–700 °C) compared to temperatures usually used in steam reforming of methane (<800 °C) [2–6]. The main reactions involved in CO2 sorption enhanced steam methane reforming are the following:

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad \Delta H_{298 \text{ K}} = 206.2 \text{ kJ/mol (1)}
\]

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H_{298 \text{ K}} = -41.2 \text{ kJ/mol (2)}
\]

The reaction (1) is highly endothermic and thermodynamically favored by high temperature and low pressure and the Water-Gas Shift (WGS) reaction (2) is favored at low temperature and has no pressure dependence. Due to the overall endothermic nature of the reaction (1), SMR needs the occurrence of the WGS reaction. Internal carbon dioxide removal by sorption on a solid would add extra heat to the reforming reaction. An optimal temperature window for CO2 sorption is 600–700 °C [7,8]. That could be of interest if CaCO3 regeneration is performed in a second reactor together with the elimination of deposited carbon produced during the hydrocarbon reforming. The use of a sorbent in the process may lead to a high hydrogen yield. In fact, the capture of CO2 shifts the balance towards a more favorable thermodynamic pathway for the production of pure hydrogen.

Several studies [3,9–12] indicate that the CaO-based materials have been highlighted as the solid sorbents in the capture of CO2 because of their favorable thermodynamic and chemical properties. The main problem with CaO is the strong decrease in the sorption capacity after multiple carbonation–calcination cycles. Sintering is indicated as the cause of the referred decay [10,13,14]. Another cause can be related to the formation of a non-porous calcium carbonate layer on the CaO grain’s surface. This phenomenon limits the diffusion of CO2 to the bulk of the grain. Thus, the exothermic reaction of carbonation can be characterized by two steps: an initial step of CO2 sorption controlled by kinetics which is followed by a slower second step controlled by CO2 diffusion in CaO and CaCO3 [15].
Several strategies are reported in the literature to prevent the decrease in sorbent efficiency due to sorption cycles and diffusion effects: optimization of calcination conditions [16,17], hydration of the sorbent [18] or deposition of calcium oxide on an inert support [4,19]. Thus, CaAl2O4 [20,21], Ca3Fe2O5 [22] or Ca12Al14O33 (magnete) [24,23,24] have been tested for CO2 sorption with CaO excess. Ca12Al14O33 has no CO2 sorption property but presents a large surface area and provides stable network inhibiting deactivation of CaO by sintering. Ca12Al14O33 appears to be an appropriate candidate to support CaO. The properties (surface area, pore volume) of these materials are strongly dependent on the synthesis method. Previous work describes the synthesis by hydration and calcination processes [9], coprecipitation [25], mixed-precipitation [26], mechanical mixing [27,28] and sol-gel process [29]. Nickel, the metal generally used in steam reforming, can be added to the sorbent CaO–Ca12Al14O33 for hydrocarbon reforming and CO2 sorption [30].

The present work proposes a new method for the preparation of CaO–Ca12Al14O33 supports with different Ca/Al ratios by microwave assisted self-combustion. This is a low cost, time-saving method with efficient preparation [31]. Then, Ni–CaO–magnete bi-functional materials (catalysts and sorbents) for CO2 sorption enhanced steam methane reforming were prepared by wet impregnation of Ni on the sorbent prepared by microwave assisted self-combustion. These bi-functional materials were tested in SMR at a low temperature (650 °C) and H2O/CH4 ratio of 3 with CO2 capture (SE-SMR). Some studies in WGS reaction are performed after SE-SMR to prove the efficiency of the catalysts for this reaction.

2. Experimental

2.1. Sorbent preparation

The samples with CaO to Ca12Al14O33 weight ratios of 75/25 and 90/10 (CA75MM and CA90MM) were prepared employing a microwave assisted self-combustion method (MM) using urea excess in the presence of ammonium nitrate. The precursors were aluminum nitrate [Al(NO3)3·9H2O—Merck], calcium nitrate [Ca(NO3)2·4H2O—Merck], urea [CO(NH2)2—Merck], and ammonium nitrate [NH4NO3—Merck]. Nitrates were chosen for synthesis because of their water solubility, low fusion temperature, and low cost. Urea has the advantage of being commercially available. It is relatively inexpensive and offers high heat generation which is important for the crystallization of the desired phases. The ammonium nitrate ensures reaction uniformity allowing all the reactants to decompose at the same time. The MM method could be of interest from an economical point of view (short preparation time, energy gains) but implies the development of an appropriate microwaves furnace for the preparation at an industrial scale.

Employing a microwave assisted self-combustion method, the aluminum, calcium and ammonium nitrates, also called oxidants, were mixed in a Becker type Pyrex with the reducing agent (urea), also known as fuel. After 10 min of stirring on a heating plate to 70 °C, the aqueous suspension was placed in a conventional microwave oven with an output power of 800 W and a frequency of 2.45 GHz until spontaneous ignition. The resulting powder was calcined at 900 °C for 1.5 h with a heating rate of 10 °C min⁻¹ then sieved at around 100 μm.

As an example, the CA75MM sorbent (75%CaO–25%Ca12Al14O33) was prepared as follows: 1.56 × 10⁻² mol of calcium nitrate, 2.60 × 10⁻³ mol of aluminum nitrate, 6.50 × 10⁻³ mol of urea and 1.25 × 10⁻¹ mol of ammonium nitrate were mixed in order to prepare 10 g of the proposed material.

Sorbents were also prepared using a natural precursor (Calcite) and aluminum nitrate (LM method) [9]. This method uses calcination and hydration processes. The natural calcite (CaCO3), ARMIL Mineração do Nordeste—Brazil, was used as the calcium oxide (CaO) precursor and submitted to calcination at 900 °C for 2 h. 7.11 g of aluminum nitrate nonahydrate (Al(NO3)3·9H2O—98.0% ALFA Aesar) and 6.55 g or 17.8 g of powdered calcium oxide were added to a mixture of 2-propanol (32.5 mL or 38.6 mL) and distilled water (190 mL) so that the weight ratios of calcium oxide to newly formed materials (Ca12Al14O33) would become 75/25 or 90/10 wt.%.

### Table 1

<table>
<thead>
<tr>
<th>Samples–composition</th>
<th>Precursors</th>
<th>Synthesis conditions</th>
<th>Calcination</th>
<th>Nomenclature</th>
</tr>
</thead>
<tbody>
<tr>
<td>75%CaO–25%Ca12Al14O33</td>
<td>Al, Ca nitrates</td>
<td>Precursors in the presence of fuel (urea)⁹</td>
<td>RT to 900 °C/1.5 h 10 °C min⁻¹</td>
<td>CA75MM or CA90MM</td>
</tr>
<tr>
<td>or 90%CaO–10%Ca12Al14O33</td>
<td>Al nitrate and calcined calcite</td>
<td>Mixing of the precursors in water and propanol, heating then drying⁸</td>
<td>RT to 900 °C/1.5 h 10 °C min⁻¹</td>
<td>CA75LM or CA90LM</td>
</tr>
<tr>
<td>75%CaO–25%Ca12Al14O33</td>
<td>Ni, Al, Ca nitrates</td>
<td>Ni impregnation of CaO then drying</td>
<td>Ni–CaO</td>
<td>Ni–CaO</td>
</tr>
<tr>
<td>or 90%CaO–10%Ca12Al14O33</td>
<td>Calcined calcite and Ni nitrate</td>
<td>Ni impregnation of CaO then drying</td>
<td>Ni–Ca75MM or Ni–Ca90LM</td>
<td>Ni–Ca75MM or Ni–Ca90LM</td>
</tr>
<tr>
<td>5%Ni–CA75MM</td>
<td>Crude calcite and Ni nitrate</td>
<td>Ni impregnation of CaO then drying</td>
<td>5%Ni–CA75LM or 5%Ni–CA90LM</td>
<td>5%Ni–CA75LM or 5%Ni–CA90LM</td>
</tr>
<tr>
<td>or 5%Ni–CA90MM</td>
<td>Ni, Al and Ca nitrates</td>
<td>Ni impregnation of CaO then drying</td>
<td>Ni impregnation of Ca75MM and Ca90MM then drying</td>
<td>5%Ni–CA75LM or 5%Ni–CA90LM</td>
</tr>
<tr>
<td>5%Ni–CA75LM</td>
<td>CaO</td>
<td>Ni impregnation of Ca75MM and Ca90MM then drying</td>
<td>RT to 750 °C/4.0 h 3 °C min⁻¹</td>
<td>5%Ni–CA75LM or 5%Ni–CA90LM</td>
</tr>
<tr>
<td>or 5%Ni–CA90LM</td>
<td>CaO</td>
<td>Ni impregnation of Ca75MM and Ca90MM then drying</td>
<td>RT to 750 °C/4.0 h 3 °C min⁻¹</td>
<td>5%Ni–CA75LM or 5%Ni–CA90LM</td>
</tr>
</tbody>
</table>

RT: room temperature; x% = x wt.%.

⁹ Microwave assisted self-combustion method (MM synthesis).

⁸ Method based on the literature (LM synthesis).
Table 1 shows the nomenclature of the prepared samples as well as the conditions for the synthesis.

2.3. Catalysts’ characterization

The catalysts were characterized by X-ray diffraction (XRD) using a Bruker D8-Advance diffractometer (Cu Kα radiation, with 40 kV and 30 mA). The diffraction powder patterns were obtained in the angular range of 10–90° using step-scanning mode (0.02°/step) with a counting time of 2 s/step. The average crystallite size of metallic nickel and calcium oxide was calculated from the broadening of the main diffraction rays using the Scherrer equation for the catalysts which underwent a reduction or the reactivity test.

The nitrogen adsorption isotherms allow the determination of specific surface area by means of the BET method (Brunauer, Emmett and Teller) on a Micrometrics Tri Star 3000 surface area analyzer. The catalysts were degassed overnight at 250 °C before being analyzed.

Temperature-programmed reduction (TPR) was carried out on a Micromeritics AutoChem II to study the reducibility of the catalysts. A mass of 50 mg was placed in a quartz U-tube (6.6 mm internal diameter) and submitted at a total gas flow of 50 mL min⁻¹, consisting of a mixture of 90% argon and 10% hydrogen. The heating rate, from room temperature to 900 °C, was 15 °C min⁻¹. A thermal conductivity detector (TCD) permitted the quantitative determination of hydrogen consumption.

2.4. Catalytic tests and ability to capture CO₂

A TGA Q500 thermal gravimetric analysis equipment was used for the carbonation and calcination experiments. 5–10 mg of catalyst was placed in a platinum/rhodium sample cup and heated at 800 °C under helium flow (10 mL min⁻¹) for 10 min to remove adsorbed water and CO₂. Then, the temperature was decreased to 650 °C and the gas mixture was changed to a 5 mL min⁻¹ CO₂ flow (10% in He). The sorption duration was 30 min, following by desorption at 800 °C for 10 min under a 10 mL min⁻¹ pure He flow. Multiple cycles, consisting of sorption and desorption steps, were repeated to test the ability of sorbents to keep their CO₂ sorption capacity.

The experiments of SE-SMR were carried out at 650 °C during 15 h. The operating conditions for cyclic stepwise SE-SMR over Ni/CAO–Ca₁₂Al₁₄O₃₃ were as follows (feed flow rates under normal conditions):

**Condition 1:** Ar = 26 mL min⁻¹ gcat⁻¹, CH₄ = 1.0 mL min⁻¹ gcat⁻¹ and H₂O = 3.0 mL min⁻¹ gcat⁻¹ (H₂O/CH₄ = 3), 1.0 g of catalyst (ratio of sorbent to methane equal to 0.75 g min mL⁻¹ and 0.90 g min mL⁻¹ for 75% and 90% CaO, respectively).

**Condition 2:** Ar = 26 mL min⁻¹ gcat⁻¹, CH₄ = 1.0 mL min⁻¹ gcat⁻¹ and H₂O = 3.0 mL min⁻¹ gcat⁻¹ (H₂O/CH₄ = 4), 2.5 g of catalyst (ratio of sorbent to methane equal to 1.88 g min mL⁻¹ and 2.25 g min mL⁻¹ for 75% and 90% CaO, respectively).

Water was injected using a syringe pump. The outlet gas was analyzed by means of gas micro-chromatography apparatus equipped with two modules: (1) using a molecular sieve column for the separation of CH₄, H₂ and CO and (2) using a HayeSep column for the separation of CH₄ and CO₂. Before the reaction test, the materials were reduced in a 30%H₂/Ar flow at 800 °C for 1 h at a constant heating rate of 10 °C min⁻¹. The flow rate of H₂ was then cut and the temperature decreased to 650 °C to add water and CH₄ in a ratio of 3.

For the study of Water Gas Shift reaction, the CH₄ flow was substituted by a CO flow (H₂O/CO ratio of 1) after 20 h of SE-SMR tests. In all the experiments, catalytic performances were evaluated by CH₄ conversion and H₂, CO, CO₂, and CH₄ molar fractions were calculated as follows:

\[ \text{Conversion(} \text{CH}_4 \text{)}(\%) = \frac{(\text{CH}_4)_{in} - (\text{CH}_4)_{out}}{(\text{CH}_4)_{in}} \times 100 \]  \hfill (4)

\[ \text{Molar Fraction } X_n = \frac{(Ax_1 f_n)}{(Ax_1 f_1) + (Ax_2 f_2) + (Ax_3 f_3) + (Ax_4 f_4)} \]  \hfill (5)

X: product; A: peak area; f: response factor and n: variation 1–4 for the four compounds (H₂, CO, CO₂, CH₄).

![Fig. 1. XRD patterns of samples: (a) Ni-CA75MM, (b) Ni-CA75LM, (c) Ni-CA90MM, (d) Ni-CA90LM and (e) Ni-CaO.](image)

![Fig. 2. Temperature-programmed reduction (TPR) profiles of the catalysts.](image)
Table 3
Ni crystallite size of the catalysts prepared by different methods after reduction.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Crystallite size after reduction (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-CA75MM</td>
<td>22.3</td>
</tr>
<tr>
<td>Ni-CA90MM</td>
<td>20.5</td>
</tr>
<tr>
<td>Ni-CA75LM</td>
<td>19.4</td>
</tr>
<tr>
<td>Ni-CA90LM</td>
<td>20.5</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Characterization of sorbents and catalysts

3.1.1. XRD

X-ray diffraction patterns of the catalysts (Ni-CA75MM, Ni-CA75LM, Ni-CA90MM, Ni-CA90LM and NiO-CaO) are shown in Fig. 1.

The structure phases of NiO (JCPDS File No. 73-1519, with space group Fm-3m, 2 = 43.39°), CaO (JCPDS File No. 78-0649, with space group Fm-3m) and Ca12Al14O33 (JCPDS File No. 48-1882, with space group I-43d) were observed. For a comparison, a standard (Ni-CaO) was prepared. According to Fig. 1, no formation of solid solution between NiO and CaO nor NiAl2O4 spinel phase was detected. NiO and CaO phases were easily detected.

Preparation methods and calcination conditions ensure the selective formation of Ca12Al14O33. No diffraction ray corresponding to another Ca–Al phase such as Ca3Al2O6, CaAl2O4, CaAl4O9 or CaAl12 O18 was observed. After Ni nitrate impregnation and calcination, neither spinel-type (NiAl2O4) nor hydrated structures Ca(OH)2 were identified, irrespective of the preparation method used. The absence of those crystalline phases in the catalysts is important for both the CO2 sorption and the steam methane reforming activity [32].

3.1.2. BET

Table 2 shows the sorbents and catalysts surface area.

The surface areas of the LM sorbents (CA75LM and CA90LM) are higher than those of MM sorbents (CA75MM and CA90MM) due to the hydration stage used in the preparation. Previous studies [18] report that the addition of water in the preparation stage of the sorbents may be responsible for producing regular hexagonal crystallloid Ca(OH)2 which becomes porous CaO during calcination at 900 °C and leads to an increase in surface area.

Such phenomenon also occurs during the impregnation of the support with Ni salt. Thus, surface area values of the catalysts prepared via wet impregnation of the support (MM and LM methods) are significantly higher than the sorbents surface prepared employing the MM method. The difference of the BET surface between Ni–CA75LM and Ni–CA90LM and between Ni–CA75MM and Ni–CA90MM is due to the amount of CaO present in the samples.

Irrespective of the preparation method, the surface areas of the catalysts are similar (Ni–CA75MM and Ni–CA75LM or Ni–CA90MM and Ni–CA90LM) within experimental error even if the initial surface areas of the supports are different. This is due to the support impregnation by a Ni salt aqueous solution for the MM catalysts and, as indicated before, to the production of porous CaO after calcination.

3.1.3. TPR

The TPR profiles of Ni catalysts are shown in Fig. 2.

The TPR profiles of the catalysts prepared by impregnation of the sorbents with an excess of CaO obtained by MM are shown in Fig. 2 (curves a and c). The maximum reduction peak is between 560 and 620 °C. A slight shoulder appears between 420 and 500 °C which can be considered as the result of the reduction of free NiO. At high temperature (750–800 °C) a small reduction peak, probably assigned to the spinel-like structure NiAl2O4, can be observed (not seen by XRD). This phase may have been formed during preparation or during TPR. The first and last signals are always of low intensity. The main signal is larger and corresponds to the reduction of nickel in strong interactions with CaO and Ca12Al14O33. It can be noticed that higher CaO excess gives the lowest reduction peak temperature (560 compared to 620 °C). This implies that NiO–Ca12Al14O33 interactions are stronger than a NiO–CaO interaction which is confirmed by the curve 2e (Ni–CaO) where the maximum of NiO reduction is located at 550 °C.

TPR profiles of LM catalysts are different (curves b and d). There is a shift of the main peak towards higher temperatures (750 °C) which indicates stronger metal–support interactions. There is no free NiO. However, there are possible Ni–Al oxide interactions. The difficulty of the reduction of the LM catalyst may have an influence on their reactivity since only a partial reduction of the sample would occur at 600–700 °C.

The diffraction patterns of catalysts after the TPR experiments (not given) show well defined diffraction rays of metallic nickel (JCPDS File No. 87-0712, with space group Fm-3m), CaO and Ca12Al14O33. The average crystallite size of metallic nickel (Table 3) is about 19–23 nm for all the samples (Ni–CA75MM, Ni–CA90MM, Ni–CA75LM, Ni–CA90LM and Ni–CaO) prepared using different methods.

Fig. 3. Comparison of cyclic CO2 sorption capacity on the sorbents (left) and catalysts (right) (CO2 sorption: 650 °C, 30 min, 10% CO2/He; desorption: 800 °C, 10 min, 100% He).
3.2. CO₂ sorption experimental results

Fig. 3 shows the CO₂ sorption capacity of the sorbents (left) and catalysts (right) after five carbonation/calcination cycles. The sorption capacity was defined as a fraction of the experimental amount of CaO (total carbonation) and the theoretical value of free CaO in the material.

After five sorption/calcination cycles, the CO₂ sorption capacity of the sorbents CA90MM, CA75MM, CA90LM and CA75LM reached values of 17.0, 27.0, 39.0, and 43.0%, respectively.

During the five cycles both CA75MM and CA90MM samples showed a slight increase in sorption capacity. The CA90MM sorbent exhibits a lower performance than the CA75MM sorbent due to the more important formation of a CaCO₃ layer which blocks the CO₂ sorption on CaO up to the heart of the grain. CA75LM and CA90LM sorbents showed higher sorption capacity than those prepared by microwaves assisted self-combustion (CA75MM and CA90MM). The hydration process linked to the preparation method had a positive effect on the surface area and, consequently, increased the sorption capacity of the LM sorbents.

After Ni impregnation, the Ni–CA90MM, Ni–CA90LM, Ni–CA75LM and Ni–CA75MM samples reached a CO₂ sorption capacity of 36.0, 36.0, 41.0 and 47.0%, respectively.

During the five cycles, the Ni–CA75MM catalyst showed a higher sorption capacity compared to catalyst with CaO excess (Ni–CA90MM) for the same reason as discussed for the CA75MM and CA90MM sorbents. The presence of Ni greatly improves the sorption properties (Ni–CA75MM and Ni–CA90MM compared to CA75MM and CA90MM, respectively). Ni–CA75MM showed a slightly higher sorption capacity than Ni–CA75LM which is contrary to lone sorbents. The sorption capacity improvement after Ni salt impregnation (Ni–CA75MM compared to CA75MM) is related to the increase in BET surface area (Table 2) and due to the hydration process. Martavaltzi et al. [33] also pointed out that the presence of NiO helped to optimize the CO₂ sorption capacity.

Irrespective of the preparation method, the presence of Ca₁₂Al₁₄O₃₃ enhances sorption capacity (compared to the Ni–CaO catalyst). This is in agreement with the BET surface area data (Table 2).

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accordance with a more appropriate dispersion of the calcium oxide phase between the calcium aluminate grains preventing the agglomeration of both CaO (responsible for CO₂ capture) and CaCO₃.

Sorption capacities of Ni–CA75MM and Ni–CA75LM were evaluated using a larger number of sorption/desorption cycles in order to verify the stability of the sorption capacity over a long period. Fig. 4 shows the performance over 30 cycles of carbonation/calcination.

A similar decay in sorption capacity was observed for the two preparation methods (MM and LM). After 24 cycles, CO₂ sorption reaches 35% and 29% for Ni–CA75MM and Ni–CA75LM, respectively, and then stabilizes. Previous studies have already shown the stability of CaO in repeated sorption–desorption cycles due to the use of Ca₃Al₂O₄S₃ in the matrix [4,9].

### 3.3. Activity for sorption enhanced steam methane reforming (SE-SMR)

Fig. 5 shows the performance of the catalysts in SMR enhanced by CO₂ sorption.

The SMR enhanced by CO₂ sorption process is divided into two steps (Fig. 5), in which the total time of the first depends on the properties of the sorbent (sorption capacity and sorption kinetics) as well as the operating conditions [2].

According to Fig. 5a, the Ni–CA75MM catalyst shows a breakthrough time for CO₂ equal to 2 h (first step). In the first step, hydrogen alone is present as product in the gas phase and the conversion of CH₄ is 100%. The entire CO produced during steam reforming is oxidized into CO₂ which is completely sorbed. The activation of the three reactions of the process (reforming reaction, water gas shift and carbonation) occurs. CO₂ sorption enhances methane and CO conversion; H₂ increases which is in agreement with the hypothesis based on the shift of the equilibrium of the steam reforming and water gas reactions.

A decrease in the formation of hydrogen associated with an increase in CO, CO₂ and methane is then observed (second step). This corresponds, exactly, to the end of the CaO carbonation (confirmed by XRD). Therefore, CO₂ sorption is no longer possible, so the steam reforming and water gas shift reactions are not shifted (reactions 1 and 2). Finally, hydrogen formation and methane conversion remain constant but at a lower level.

The Ni–CA90MM catalyst (Fig. 5b) showed a breakthrough time (1 h) for CO₂ lower than the Ni–CA75MM catalyst. This can be justified by a greater sorption capacity of Ni–CA75MM. In the second step, a sudden drop in hydrogen concentration associated with an increase in CO, CO₂ and methane is observed. The Ni–CA90MM catalyst showed a weaker performance compared to the other catalysts. That can be associated with the rapid sintering of the CaO particles or with the formation of a layer of CaCO₃ that prevents the diffusion of CO₂ and its sorption on the available CaO. With lower CaO excess (48 and 65%), the methane conversion is similar to the catalyst containing a 75% CaO excess but the breakthrough time (curves not given) is reduced to 30 and 50 min, respectively.

The Ni–CA75LM catalyst (Fig. 5c) showed a breakthrough time for CO₂ (first step) similar to the Ni–CA75MM catalyst and similar CO₂ sorption capacity. However, after this period its activity regularly decays over time.

Fig. 5d shows the performance of the NiO–CaO catalyst. This figure clearly shows the importance of the Ca₃Al₂O₄S₃ phase. The agglomeration of CaO for Ni–CaO catalyst (Table 4) in relation with a strong decrease in CO₂ sorption (Fig. 3) can be the cause of the low performance of this catalyst. In fact, this catalyst is the only one where CaO particles size grows during the catalytic test.

To study the aging of the catalyst, long term catalytic tests were also performed. Fig. 6 shows the behaviour of the catalyst Ni–CA75MM during 50 h of reaction. The greatest time observed for the first step is due to the increase in the sorbent/methane ratio compared to the previous reaction conditions (2.5 times).

After the first step (saturation of CaO), hydrogen production was stable for a period of 50 h (second step) when the reaction is carried out using the catalyst obtained using the MM method. CO and CO₂ formation and methane conversion also remain constant during this time.

The after reactivity characterizations seem to point to the fact that activity decay after 7 h is probably not due to the increase in Ni particles size: about 19–23 nm after reduction (Table 3) and between 22 and 29 nm after 15 h or 50 h of reaction for all the catalysts (Table 5).

Additionally, carbon deposition after testing stays at a low level. It was calculated from the profiles of temperature programmed oxidation of the residual carbon after a temperature programmed desorption of species containing CO₂ like carbonates or hydrogen carbonate (not shown). Ni–CA75MM and Ni–CA90MM showed no carbon deposition while Ni–CA75LM showed a deposition of 3.0 × 10⁻⁴ mol carbon gₗ⁻¹×mol of converted CH₄⁻¹ (at 600 °C), so, activity decay (between steps 1 and 2) would be due to the end of carbonation. To be sure that WGS reaction really occurs in the presence of the catalyst, the behaviour of Ni–CA75MM has been studied in this reaction (Fig. 7).

As soon as CH₄ has been cut, H₂ decreases and CO₂ increases abruptly, then stabilizes for a long period. The entire CO is consumed and the H₂/CO₂ ratio near 1 leads to the conclusion that the WGS reaction is catalyzed by these catalysts.

### 4. Conclusions

A new method for the preparation of Ni–CaO–mayenite bifunctional materials (catalyst/sorbent) was developed. Some synthesis

### Table 4

<table>
<thead>
<tr>
<th>Samples</th>
<th>Crystallite size before reaction (nm)</th>
<th>Crystallite size after reaction (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni–CA75MM</td>
<td>31.7</td>
<td>30.2</td>
</tr>
<tr>
<td>Ni–CA90MM</td>
<td>32.3</td>
<td>31.5</td>
</tr>
<tr>
<td>Ni–CA75LM</td>
<td>31.4</td>
<td>30.8</td>
</tr>
<tr>
<td>Ni–CA90LM</td>
<td>32.6</td>
<td>31.7</td>
</tr>
<tr>
<td>Ni–CaO</td>
<td>31.1</td>
<td>39.7</td>
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</table>

### Table 5

<table>
<thead>
<tr>
<th>Samples</th>
<th>Test duration (h)</th>
<th>Crystallite size after reaction (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni–CA75MM</td>
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<td>27.9</td>
</tr>
<tr>
<td>Ni–CA90MM</td>
<td>15</td>
<td>28.3</td>
</tr>
<tr>
<td>Ni–CA75LM</td>
<td>15</td>
<td>22.6</td>
</tr>
<tr>
<td>Ni–CA90LM</td>
<td>15</td>
<td>25.3</td>
</tr>
</tbody>
</table>
The catalyst was the most active and stable in CO2 sorption enhanced steam methane reforming (SMR) with simultaneous sorption of CO2. The results show that the formation of hydrogen can be optimized via steam methane reforming with simultaneous CO2 capture using CaO dispersed on an adequate support. There is an optimal CaO/support ratio and the best compromise corresponds to an excess of 75% of CaO. The CaO carbonation shifts the equilibrium of the Water Gas Shift and improves both the productivity of SMR and the selectivity to hydrogen (100% hydrogen production). After total carbonation of the CaO, the methane conversion decreases, and CO and CO2 appear in the gas phase. The Ni–CA75MM catalyst was the most active and stable in CO2 sorption enhanced steam methane reforming, even at an unusually low temperature (650 °C).

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References