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Development of synthetic Ca-based CO₂ sorbents for sorption enhanced reforming coupled to Ca/Cu chemical loop

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Abstract

Sorption Enhanced Reforming (SER) is a very promising option that allows H₂ production coupled with capturing CO₂ by sorption. The present research work focus in the sorbent point of view and several synthetic materials with a high CO₂ absorption capacity and chemically and mechanically stable during multi-cyclic operation (at least 40 calcination-carbonation cycles and 100 cycles in some cases) under the typical SER process conditions have been developed. Two different synthesis routes (co-precipitation and mechanical mixing) have been followed trying to evaluate the effect of two different inert supports (magnesium oxide and mayenite) on the evolution of the CO₂ carrying capacity of the materials. Also, sorbents have been synthesized with different morphologies (powder and particles) and sizes (from 100 microns up to 2 mm) in order to test their reactivity and mechanical suitability for large scale reactor system operation. Synthetic dolomite with a molar CaO/MgO ratio of 2:1 synthesized by co-precipitation method exhibited very stable performance for 100 consecutive carbonation/calcination cycles and a residual CO₂ carrying capacity of 0.29 gr_{CO₂}/gr_{calcined sorbent}. Also a very promising result has been obtained for this sorbent mixed with a commercial catalyst in a preliminary SER experiment that yield a H₂ production of 92 % vol. (d.b.).

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Keywords: CO₂ capture; SER; carbonation/calcination cycles; Ca-based sorbents; inert support

1. Introduction

Hydrogen demand by chemical and energy industries is continuously growing and steam methane reforming is the most extended hydrogen production process with high CO₂ emissions associated. Nowadays, CO₂ capture is a

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promising option to decrease global CO₂ emissions and there is great interest worldwide in developing new CO₂ capture technologies aiming at reducing the energy penalty. However, combined strategies of hydrogen production with CO₂ capture and materials able to work under such process conditions are still at a very early stage of development. Sorption Enhanced Reforming (SER) is a very promising option that allows capturing CO₂ by sorption while sorbent regeneration can be done following different routes. A recent invention [1] based on the fundamentals of oxygen and heat transfer in chemical looping processes proposes to use Ca-based CO₂ sorbents in combination with Cu oxides with exothermal reduction. Ca-Cu solids coupled to a proper steam reforming catalyst will allow hydrogen production with in situ CO₂ capture and successive sorbent regeneration in cyclic operation [2]. Up to now, one of the most important challenges is to find appropriate materials that withstand the typical SER process coupled to Ca-Cu process conditions working in multi-cycle operations (reforming/oxidation/reduction).

From the sorbent point of view, it must show a stable sorption capacity during cycles, low-cost manufacture, fast reaction kinetics, mechanical stability and sintering resistance. Although natural carbonates, e.g. limestone or dolomite seem to be the best candidates given their low cost and its high availability, they show a pronounced decay in CO₂ sorption capacity during repeated cycling due to sintering and modification of particles porous structure.

Some methods were proposed to solve this problem, including (i) reactivation of CaO with hydration method [3] and superheating of Ca(OH)₂ [4]; (ii) pre-activation [5] and self-activation [6] or post-activation [7]; (iii) sorbent doping [8] and (iv) synthetic sorbents [9]. More details about these methods can be found in a very extensive review published by Liu et al. (2012) [10]. Among reviewed methods for improving sorbent reactivity, adding inert support into CaO has been studied extensively including the addition of MgO, MgAl₂O₄, Ca₁₂Al₁₄O₃₃, SiO₂, CuO, CoO, Mn₂O₃, CaTiO₃, etc. Also various preparation methods to incorporate the inert support particles into CaO particles, such as wet chemistry, dry or wet mixing, sol-gel, flame synthesis and template synthesis are included in the review [10].

The present research work focus on development of synthetic materials with a high CO₂ absorption capacity and chemically and mechanically stable during multi-cyclic operation (at least 40 calcination-carbonation cycles and 100 cycles in some cases) under the typical SER process conditions. Two different synthesis routes (co-precipitation and mechanical mixing) have been followed trying to evaluate the effect of two different inert supports (magnesium oxide and mayenite) on the evolution of the CO₂ carrying capacity of the materials. Also, sorbents have been synthesized with different morphologies (powder and particles) and sizes (from 100 microns up to 2 mm) in order to test their reactivity and mechanical suitability for large scale reactor system operation. Best performance solids will be selected for scaling up and operation in multi-cycle reforming/oxidation/reduction tests mixed with a NiO-based reforming catalyst.

2. Experimental

2.1. Synthesis of CaO-based CO₂ sorbents

Two different synthesis routes have been used for producing CO₂ sorbents aiming to disperse the Ca on the support to avoid the typical sintering of natural Ca based sorbents. In the first route, MgO is used to dilute the CaO in the sorbent emulating natural dolomites [11,12]. In the second route, calcium aluminate cement in different proportion is used as binder. The alumina present in the cement partially reacts with CaO to generate mayenite (Ca₁₂Al₁₄O₃₃) that has proven to be an excellent support for synthetic CO₂ sorbents [8,13].

The first synthesis route aims the production of materials that emulate the structure of natural occurring dolomites in which the MgO, inert for the carbonation reaction in the range of temperatures of interest, acts as a stable framework reducing the sintering of CaO along calcination/carbonation cycles. Synthetic dolomite sorbents with different CaO:MgO molar ratios were prepared using a co-precipitation method [12]. Calculated amounts of Ca(NO₃)₂•4H₂O and Mg(NO₃)₂•6H₂O were dissolved in deionised water giving 50 ml of solution with a total concentration of 3 M. A 2M solution of (NH₄)₂CO₃ was used as precipitation agent and added drop wise to the mixture under vigorous stirring at room temperature. A pH value of 9 was kept constant by the drop wise addition of 30 % NH₃ aqueous solution. The precipitates were aged for 2 hours and subsequently washed with water during vacuum filtration. The filter cakes were then oven-dried at 120 °C for 12 hours and calcined in a muffle furnace under air at 875 °C for 2 hours. Four sorbents with different active phase to support molar ratios (5:1, 3:1, 2:1 and

1:1) and also pure CaO were prepared by this co-precipitation method. Fresh calcined materials were crushed and sieved to get a powder with a particle size less than 100 μm . In order to get the materials of interest in the Ca/Cu process that operates in fixed bed reactors, selected powder sorbents were submitted to an agglomeration process using a polyethylene glycol (PEG) 5 % wt. aqueous solution as binder. Briefly, the solid was mixed by a propeller working at 2000 rpm and binder was added drop wise up to a 35 % of total (solid + binder) weight. Particles were dried at 120 °C overnight and sieved to separate fractions with different particle diameter. Taking into account the mechanical suitability of particles for large scale reactor system operation (pressurized fixed bed reactor), two fractions (0.6-1 mm and 1-2 mm) were selected and calcined in air at 900 °C during 1 hour.

In the second synthesis route, natural limestone and calcium aluminate cement were used as raw materials for preparing the synthetic sorbent. First, natural limestone was calcined for 2 h at 900 °C, producing 55.59 wt.% of solid residue. Main components of calcined limestone were 97.85 wt.% of CaO, 0.19 wt.% of MgO and 1.92 wt.% of Na₂O. Calcium aluminate cement is a commercial product from cement industry mainly composed of aluminum, iron and calcium oxides. The materials were mechanical mixed in the correct proportions in order to get CaO contents between 60-95 % wt. Afterwards, water was added drop wise with a continuous mixing to get a homogeneous paste that was dried in a furnace at 120 °C for 12 hours crushed and sieved to obtain a powder with a particle size less than 100 μm , finally the powder materials were calcined in air at 900 °C for 2 hours. Selected materials were also agglomerated with the same procedure described previously for the synthetic dolomites with a binder solution of 5% PEG.

2.2. Characterization

Sorbents were deeply characterized in order to know textural, physical, and crystallographic parameters that can influence on the CO₂ carrying capacity and mechanical stability of the materials. In order to avoid hydrated and/or carbonated species all samples were calcined immediately before characterization at the same conditions that were used during the synthesis procedures and were stored in a desiccator. Surface area was determined by nitrogen adsorption at -196 °C in a Micromeritics ASAP-2020 analyzer. Prior to the N₂ adsorption analysis, each sample was degassed at 250 °C for approximately 3 h. The Brunauer-Emmett-Teller (BET) model was used to calculate the surface area in the P/P₀ range of 0.02 to 0.3. A picnometer AccuPyc II 1340 was used to determine sorbents density by measuring the amount of He displaced by the sample. Prior to the analysis, each sample was degassed at 130 °C in a vacuum oven. In order to estimate the solid porosity (ϵ) and the solid pore size distribution, a Hg Porosimeter Quantachrome Pore Master analyzer was used.

The crystallinity and phases composition of the synthesized sorbents were evaluated using X-ray powder diffraction (Bruker, AXS D8 Advance, Cu K α radiation, equipped with a Lynxeye superspeed detector operated at 40 mA and 40 kV). Each sample was scanned in the 2 θ range of 15-80°. The step size was 0.02° and the scan time per step was 3 s. Particles were grinded to powder before analysis. XRD diffractograms not only allowed for phase identification but also its quantification. Rietveld analysis of the diffractograms allowed for quantification of different phases present in the sorbents. In order to check the accuracy of these measurements selected samples were also quantified by ICP-AES and a good correlation between both techniques was observed for Ca and Mg real concentrations. To define the morphology of sorbent particles (surface and cross-section), a scanning electron microscopy (SEM) using a Hitachi S-3400 N was applied. In addition, energy dispersive X-ray (EDX) analysis was used to evaluate the distribution of the different elements present in the sorbents.

2.3. Sorbent performance evaluation

Material reactivity and cyclic stability tests were performed using a TGA analyser. Briefly, the apparatus consists of a quartz tube with a platinum basket suspended from it, inside a two-zone furnace. The furnace can be moved up and down by means of a pneumatic piston. The position of the furnace with respect to the platinum basket allows alternation between calcination and carbonation conditions. The temperature and sample weight were continuously recorded on a computer. The reacting gas mixture can be regulated by mass flow controllers and fed in through the bottom of the quartz tube. Steam was generated by external electric heating of the water flow controlled by a liquid mass flow controller and then introduced into the reaction atmosphere. Each sample was carbonated for 15 minutes

in 15% CO₂/15% H₂O/70% N₂ at 650 °C up to reach at least 40 calcination-carbonation cycles (100 cycles in some cases). The sorbent calcination was performed at 900 °C in a 70% CO₂ in air.

2.4. Catalyst+sorbent SER performance evaluation

To assess the performance of the best sorbent obtained in this work, a mixture of sorbent and a commercial reforming catalyst was tested in a quartz micro-fixed bed reactor with an internal diameter of 6.8 mm under typical Sorption Enhanced Steam Methane Reforming conditions. The reactor is located in a cylindrical electrically heated oven controlled by a PID controller and a thermocouple placed on the surface of the sample. This system is capable to allocate 800 mg of material in the isothermal area of the reactor where a mixture of 46 mg of a commercial Ni-based reforming catalyst and 690 mg of Ca-based CO₂ sorbent were placed. The system allowed feeding CH₄, H₂, O₂, Ar and water by means of calibrated mass flow controllers. Water was mixed with the gas stream and evaporated passing through a tube inside a cylindrical electric furnace. After the fixed bed, the gases passed through a recovery system to condense water. Finally, aliquots of the gas stream were analyzed on line using a quadrupole spectrometer (Omnistar, Pfeiffer Vacuum) The following masses were monitored: m/z =2 for H₂, m/z =15 for CH₄, m/z=18 for water, m/z = 28 for CO, m/z=32 for O₂ m/z = 40 for Ar and both m/z= 28 and 44 for CO₂. The experiments were performed at a temperature of 650 °C, with a Steam-to-Carbon ratio of 4 and a weight ratio calcined sorbent/reforming catalyst (Z) of 15.

3. Results and discussion

3.1. Characterization of CaO-based CO₂ sorbents

Main textural and physical properties of sorbents prepared by the co-precipitation method are presented in Table 1. Pure CaO prepared by the co-precipitation method shows the lowest surface area, density and porosity whilst the synthetic dolomite with a ratio 1:1 present the highest values. The presence of MgO inert phase seems to favor the development of a rich structure with surface areas ranging from 16 m²/g to 26 m²/g, higher than that of natural CaO (12-15 m²/g) and high porosities ranging from 0.75 to 0.78. These results are in line with other well dispersed CaO-MgO materials published by several authors and using different preparation methods like wet-mixing (up to 25 m²/g) [11], co-precipitation (2-35 m²/g) [12], sol-gel auto-combustion (28 m²/g) [14]. The agglomeration process reduces both the surface area (12 m²/g) and the porosity of the material (0.5).

Table 1. Main textural and physical properties of sorbents prepared with the co-precipitation method.

Sorbent	S _{BET} (m ² g ⁻¹)	Particle density (gcm ⁻³)	ε	CaO crystallite size (nm)	MgO crystallite size (nm)
CaO	15.65	2.21	0.53	-	-
CaO:MgO 5:1	16.75	2.94	0.76	32.5	16.3
CaO:MgO 3:1	17.49	3.19	0.78	38.5	19.6
CaO:MgO 2:1	16.51	3.24	0.75	39.9	22.8
CaO:MgO 1:1	25.87	3.28	0.78	36.9	15.9
CaO:MgO 2:1 (0.6-1.0 mm)	12.23	3.14	0.50	-	-
CaO:MgO 2:1 (1.0-2.0 mm)	11.95	3.05	0.51	-	-

The crystalline phases formed in the co-precipitation CO₂ sorbents were determined by X-ray Diffraction. Figure 1 (left) illustrates the X-ray diffraction patterns of selected CaO sorbents with different CaO:MgO molar ratios. All samples presented the characteristic reflections of CaO and MgO along with low intensity peaks of Ca(OH)₂ phase that are attributed to the absorption of moisture due to the hygroscopic nature of the materials. No mixed phase peaks were detected so the metal oxide support is inert to CaO.

Rietveld analysis of the diffractograms followed by Double-Voigt approach allowed to calculate the crystallite size of CaO phase, that was ranging between 32 and 40 nm, and MgO phase ranging from 16 to 23 nm (see Table 1).

These results are comparable with other recently published by different authors and using different synthesis methods. Liu et al. (2010) [11] published well dispersed CaO-MgO materials prepared through wet-mixing of calcium gluconate and magnesium gluconate salts showing the formation of CaO particles of ~36 and ~120 nm, with nanocrystalline domains of MgO (~9 and ~50 nm). Antzara et al. (2015) [14] have also recently published the preparation of CaO-MgO sorbents by sol-gel auto-combustion method with a CaO crystallite size of 29.5 nm.

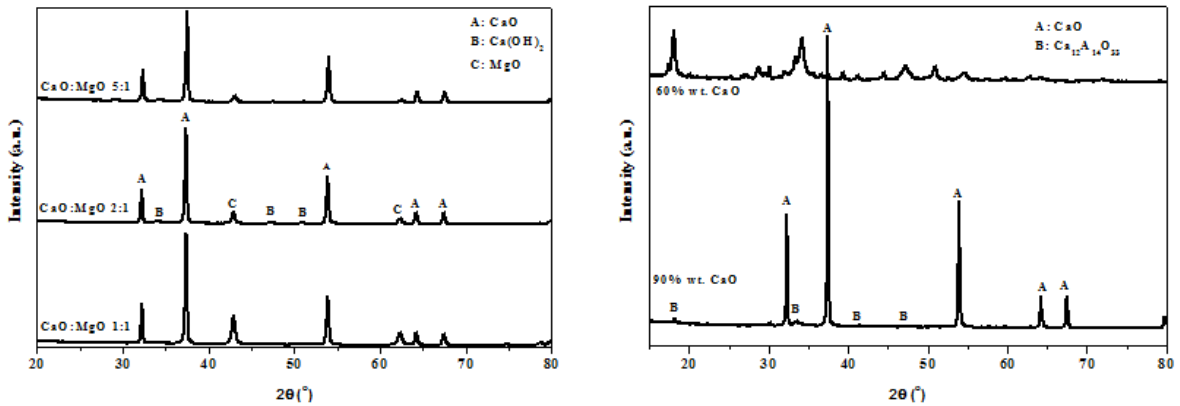


Fig. 1. X-ray diffraction patterns of selected CaO sorbents with different CaO:MgO molar ratios (left) and selected CaO/calcium aluminate cement sorbents with different CaO % wt (right).

Figure 2 shows the SEM micrograph of a particle cross-section corresponding to the synthetic dolomite CaO:MgO 2:1 with a particle size of 1.0-2.0 mm. Indicative mapping of the surface composition with EDX was performed on the same samples and is also presented in Fig. 2. The analysis confirmed the good distribution between Ca and Mg elements, indicating the suitability of the followed synthesis route for uniform dispersion of CaO and inert support in the solid particles. Thus, the finely-dispersed support among CaO particles would fully function as the metal matrix, which could effectively prevent the collapse of pore structure and further suppress the sintering of sorbent particles.

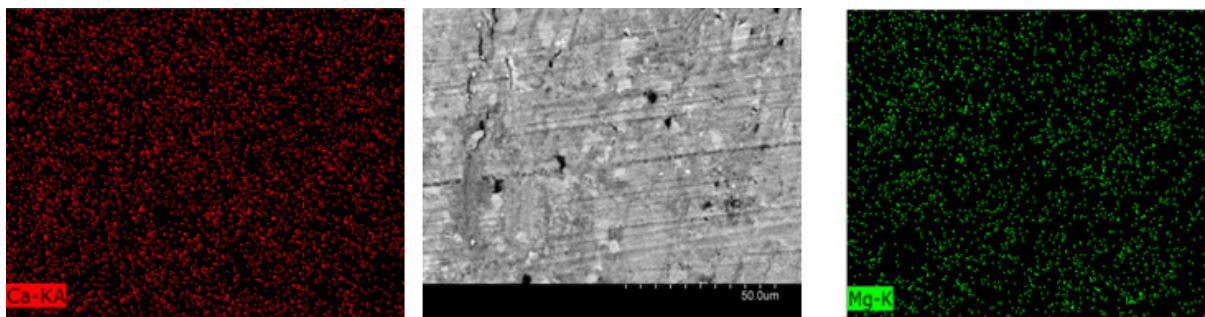


Fig. 2. Cross-section SEM micrograph (center) and EDX analysis (left Ca, right Mg) of particulate CaO:MgO 2:1 material.

Figure 3 shows some examples of the pore size distribution for the fresh calcined materials synthesized and tested in this work. The synthetic dolomites (figure 3 left), although all of them reported high and similar porosity (shown in table 1) they present some differences on the pore structure. All of them present an important pore volume in the range of pore diameters below 50 nm, that according to the literature [15,16] are typical pore diameters meaningful for reaction of CaO with CO₂, but these materials, specially the material with lower CaO content, present an

important pore volume at higher pore diameters that could be associated with the presence of MgO as it was found by Liu et al. 2010 [11]. The figure also includes the pore size distribution of one material that contains $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ as inert support (aprox. 10 % wt). This material presents a uni-modal pore size distribution function but with a wider distribution of pore diameters with an average pore size slightly over 50 nm.

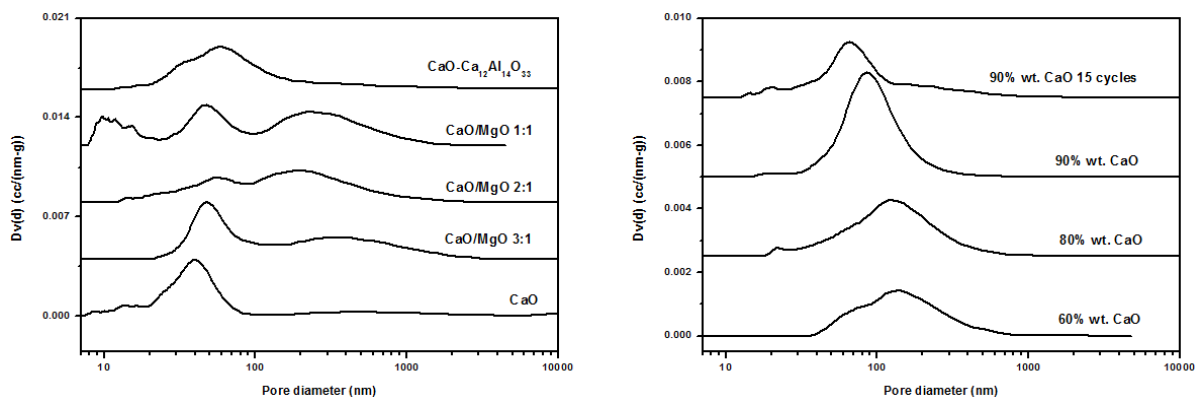


Fig. 3. Pore size distribution of the fresh materials, calcined at 900 °C in air. (Left) selected CaO sorbents with different CaO:MgO molar ratios and (right) selected CaO/calcium aluminate cement sorbents with different CaO % wt.

Main textural and physical properties of sorbents with particle size ranging from 0.6 to 1 mm prepared by the mechanical mixing method are presented in Table 2. These materials present a less developed surface area and porosity compared with the synthetic dolomites (see table 1). The higher the amount of calcium aluminate cement is in the sorbent, the less the textural properties are. Results for the sample with a 90% wt. of CaO after 15 calcination/carbonation cycles are also collected and its surface area is drastically reduced from 10.17 to 5.48 m^2g^{-1} due to the sintering effect of the active phase pointed out by the growth of the CaO crystallites from 64.7 to 76.4 nm.

Table 2. Main textural and physical properties of sorbents prepared with the mechanical mixing method.

Sorbent	S_{BET} (m^2g^{-1})	Particle density (gcm^{-3})	ϵ	CaO crystallite size (nm)
90% wt. CaO	10.17	3.12	0.56	64.7
90% wt. CaO after 15 cycles	5.48	3.20	0.49	76.4
80% wt. CaO	8.55	3.13	0.55	-
60% wt. CaO	7.11	3.16	0.54	-

The $\text{CaO-Ca}_{12}\text{Al}_{14}\text{O}_{33}$ materials present a higher mean pore diameter, around 100 nm, (Fig. 3 right) than CaO-MgO materials, that might be linked to their synthesis method as the CaO source in these materials is obtained from the calcination of powdered natural limestone. In this way, pore size distribution of the materials with a high CaO content is very similar to those that present natural lime [15,16] while the materials with higher inert content present a wider pore size distribution peaking at higher pore sizes. This fact might be associated to the increment of intermediate species other than $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ and CaO that appear in the XRD diffractogram of sample 60% wt. CaO compared with the one of sample 90% wt. CaO where only CaO and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ phases are detected (see figure 1, right). Regarding the cycled sample and its pore size distribution it can be observed that the mean peak around 100 nm has been reduced and a shoulder around 200 nm is starting to appear due to the shrinkage of the porous during the sintering process.

3.2. Evaluation of sorption capacity and stability

In a first step to determine the suitability of the materials for the Cu/Ca reforming process, the evolution of CO₂ carrying capacity of the materials with the number of reaction cycles under meaningful reaction conditions (high CO₂ partial pressure during calcination stage and steam during the carbonation stage) has been evaluated using a TGA analyzer. Figure 4 (left and right) compiles the experimental results on the evolution of CO₂ carrying capacity with the number of calcination/carbonation cycles for the materials prepared through both synthesis routes and CaO contents between 60 to 90 % wt. The figure also includes for comparison the chemical stability of a 100 % wt. CaO material prepared by precipitation, and CaO obtained directly from the calcination of natural limestone. According to the Figure 4 (left), the presence of MgO acting as inert support really improves the CO₂ carrying capacity of the materials in the long term performance, this can be extracted from the comparison between the serie obtained with the precipitated CaO and the rest of the materials that contain MgO. Among the materials that contain both MgO and CaO, it can be seen that the decay observed along the initial cycles is reduced for the materials with higher MgO content (especially material CaO:MgO with a molar ratio 1:1). This observation is coherent with the results presented by Li et al. 2013[17] that applied the Zener pinning theory to describe the inhibition of CaO grain sintering thanks to the addition of an inert support. According to those authors, the inhibition effect is dependent on the inert support size, and also on its volume fraction. In this way materials with a relatively high inert content present a lower amount of active CaO during the initial cycles, but their decay in activity is reduced with respect to materials with lower amount of inert support. Still it is important to highlight that the lifetime of these materials will comprise an important number of reaction cycles, and at this point the differences between materials disappear and as long as there is a minimum amount of inert support (for example 12.5 wt. % in the material CaO/MgO molar ratio 5:1), the sorbent performance is highly improved with respect to the material with no inert support. In general the CO₂ carrying capacity of the materials tends to stabilize over 0.25 gr_{CO₂}/gr_{calcined sorbent} with a maximum of 0.29 gr_{CO₂}/gr_{calcined sorbent} for the material CaO:MgO with a molar ratio 2:1.

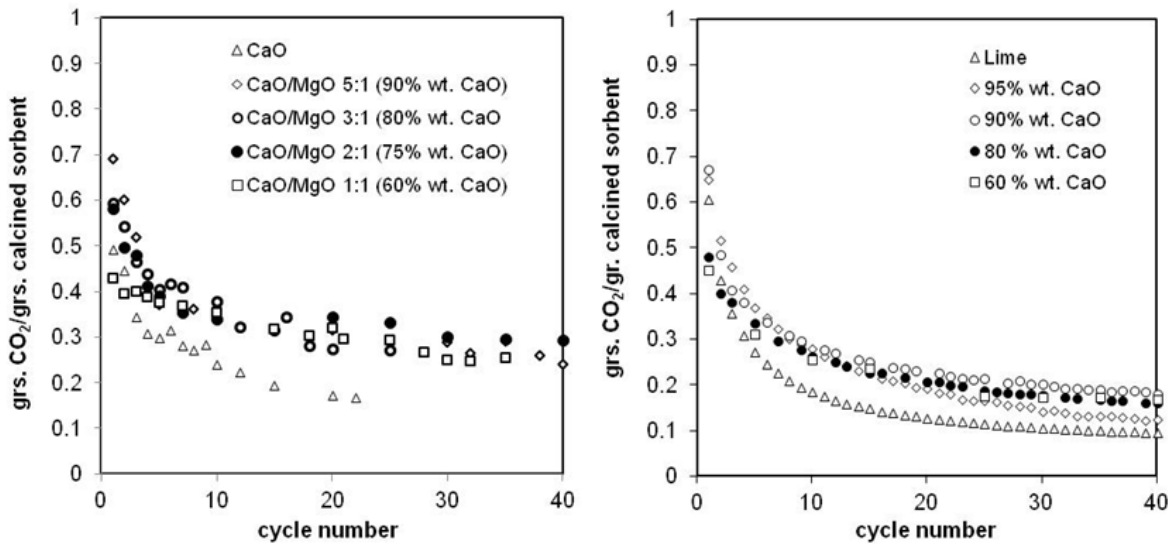


Fig. 4. CO₂ carrying capacity along calcination/carbonation cycles of sorbents based on CaO-MgO (left) and CaO-Ca₁₂Al₁₄O₃₃ (right). Carbonation at 650 °C in in 15% CO₂/15% H₂O/70% N₂ flow and calcination at 900 °C in 70% CO₂ in air flow.

Figure 4 (right) shows a similar comparison but for the materials prepared by mechanical mixing and later calcination of CaO and Ca aluminate cement. A similar trend is observed as for the co-precipitated material, with a minimum amount of inert support required to maintain sorbent activity. In this case it is clear that the activity of the material with a 5 % wt. Ca aluminate cement is very similar to that obtained with natural lime. Comparing both

types of materials the CO₂ carrying capacity of the co-precipitated material is sensibly higher than for the CaO-Ca₁₂Al₁₄O₃₃ materials (0.29 and 0.20 gr_{CO₂}/gr_{calcined sorbent} respectively) this fact could be related with the higher crystallite size (over 65 nm) that presents CaO with respect to the 30-40 nm crystallite size that present the co-precipitated materials [17]. Moreover, the presence of intermediate phases CaO·Al₂O₃ is important in the materials with higher amounts of inert support in the mechanical mixing prepared sorbents.

To prove the stability of the materials and to determine their residual capacity two of them (prepared by different synthesis route) have been tested for a long number of cycles (up to 100 cycles). The experimental data, shown in figure 5, have been fitted to Equation (1) that has been widely used in the literature to describe the evolution of sorbent CO₂ carrying capacity with the number of cycles [18].

$$X_N = \frac{1}{\frac{1}{(1 - X_r)} + kN} + X_r \quad (1)$$

This equation is analogue to a second-order catalyst deactivation equation adapted to consider the proportionality between conversion, surface area and product layer thickness through two parameters that are characteristic of every material: the sorbent deactivation constant, k, and sorbent residual capacity X_r. Those values were k=1.53 and X_r=0.27; k=0.5 and X_r=0.17 for the CaO-MgO and CaO-Ca₁₂Al₁₄O₃₃ materials respectively. Although the CaO-MgO material presented a lower initial CO₂ carrying capacity compared with the CaO-Ca₁₂Al₁₄O₃₃ one due to their different active phase contents (75 and 90% wt. CaO respectively); the sintering resistance of the material with MgO inert support is higher and therefore its residual CO₂ carrying capacity after 100 cycles is notably better compared with the mayenite inert support one (0.29 and 0.20 gr_{CO₂}/gr_{calcined sorbent} respectively).

Although, both materials would fulfill the requirements described by Fernandez et al. 2012 [19] to sustain a Sorption Enhanced Steam Methane Reforming process at large scale, CaO-MgO 2:1 sorbent was chosen as best candidate and subjected to a deeper performance analysis.

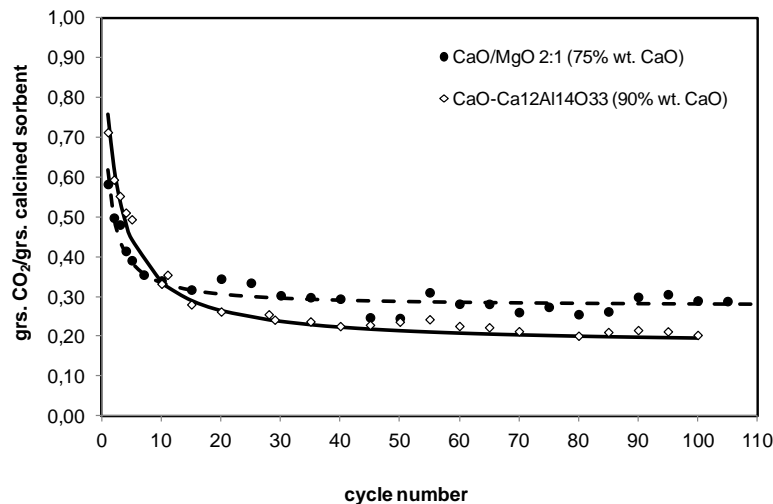


Fig. 5. CO₂ carrying capacity along calcination-carbonation cycles of most promising sorbents tested over 100 cycles. Carbonation at 650 °C in in 15% CO₂/15% H₂O/70% N₂ flow and calcination at 900 °C in 70% CO₂ in air flow.

3.3. Evaluation of CaO content and particle size on sorbent reactivity

Figure 6 shows the effects of CaO content and particle size on the CaO molar conversion (X_{CaO}) of the synthetic dolomites, where it can be observed the well known two reaction stages [20,21] related with the control by the chemical reaction during the initial fast reaction stage, followed by a second slower reaction stage which is governed by a combined control between the chemical reaction and the CO_2 diffusion through the product layer formed [16]. Through the representation of the experimental data of CaO/MgO materials in powder form ($< 100 \mu m$) with different amounts of CaO under identical conditions of carbonation temperature and CO_2 partial pressure (figure 6 left), it can be observed that the main difference between the CaO conversion curves is just the conversion level at which the transition between the two different reaction rates (or regimes) takes place. The three experimental curves present a very similar slope during the fast reaction period that is associated to the control by the chemical reaction, indicating that carbonation reaction kinetics under this initial stage might not be highly affected by the active CaO content of the material. It also can be observed that the conversion level at which the transition between reaction regimes take place is directly related with the amount of CaO present in the sorbent. And, also for analogy with the knowledge of the carbonation of CaO from natural limestone, the conversion level at which transition takes place will be related with a characteristic product layer thickness at which the contribution of the diffusion coefficient through the $CaCO_3$ formed starts to influence the carbonation reaction rate [16]. This characteristic product layer thickness at which the carbonate layer is well developed might depend on the amount of CaO present in the sorbent.

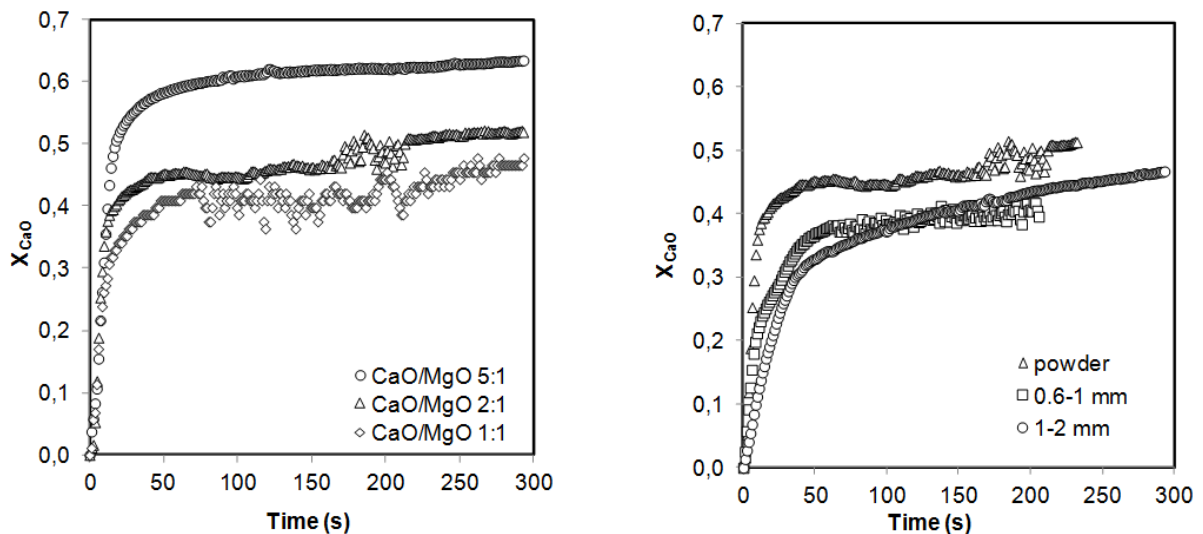


Fig. 6. Carbonation conversion curves at $650 \text{ }^\circ\text{C}$ and p_{CO_2} 15 kPa for synthetic dolomite sorbents with different CaO/MgO ratios in powder form (left) and for CaO/MgO 2:1 sorbent with different particle sizes (right).

The reactivity of particles formed by agglomeration has been also assessed. The results, as expected indicated that materials reactivity is reduced when increasing the particle size, and the CO_2 diffusion to the interior of the pore structure start to play a role for the bigger particle sizes. Still, the main features for the carbonation reaction of CaO are still present (as they are the two reaction stages) and the total sorbent conversion is not affected by particle size.

3.4. Catalyst+sorbent preliminary SER test

The joint performance of the best candidate material (CaO/MgO 2:1), and a commercial reforming catalyst has been tested under SER operation conditions described on section 2.4. The CH_4 space velocity was set at $0.75 \text{ kg } CH_4$

$\text{hr}^{-1} \text{ kg cat}^{-1}$, for a calcined sorbent to catalyst ratio of 15 (this is less than 1% Ni content in bed), and S/C of 4 at 650 °C.

Results of evolution of meaningful species in product gas composition with time are presented and compared to theoretical values of thermodynamical equilibrium in figure 7. This figure shows the three typical reaction periods in a SER reforming process: the pre-breakthrough period, where the sorbent is reacting with CO_2 and the global reaction displaces the equilibrium towards H_2 production, the transition period where the sorbent is reaching its maximum CO_2 carrying capacity and H_2 production decreases and finally the third stage where the sorbent is no longer active and typical Steam Methane Reforming gas composition is achieved [22]. Results indicate that sorbent reactivity is sufficient to sustain the SER reaction since the mixture of catalyst and sorbent is able to produce a gas stream proximal to the thermodynamical equilibrium predictions for these conditions. The H_2 concentration during the pre-breakthrough period is close to 92 % vol. (d.b. free of Ar) and small fractions of CO_2 , CO and CH_4 are observed in the product gas. The mass balance to carbon species and experimental and theoretical CO_2 concentrations in the system, allowed to determine different parameters related to sorbent performance in this experiment. The pre-breakthrough period is experimentally limited to 300 min of reaction and the CO_2 -carrying capacity showed by the sorbent in this period was $0.4 \text{ gr}_{\text{CO}_2}/\text{gr}_{\text{calcined sorbent}}$. This result corresponds to a CaO conversion (X_{CaO}) of 0.69 and a CO_2 capture efficiency of more than 99% of the maximum limited by the theoretical equilibrium (77.6 %). At this first carbonation cycle of the sorbent, a carbonation rate of $1.1 \cdot 10^{-5} \text{ kmol}_{\text{CO}_2}/\text{kg}_{\text{sorbent}} \cdot \text{s}$ was achieved. This value is comparable with the value observed in the theoretical work of Fernandez et al. [19] for a synthetic sorbent with a X_{max} of 0.4. Once the post-breakthrough period was reached, the H_2 concentration was decreased to less than 80% vol. as well as CO and CO_2 clearly increased to reach values of SMR equilibrium composition in the product gas.

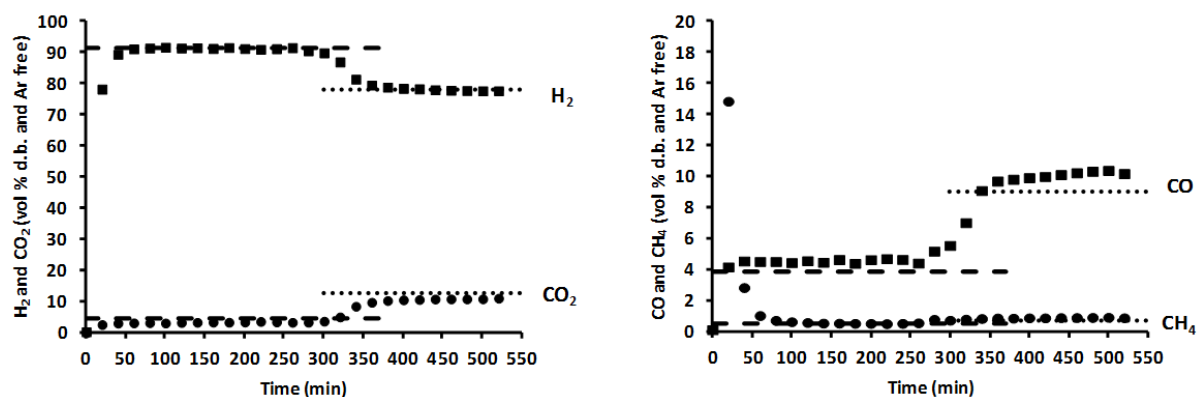


Fig. 7. Evolution of product gas composition with time, H_2 , CO , CH_4 and CO_2 % vol. (d.b. free of N_2) plotted. Experimental conditions: S/C 4, Z=15, 650 °C and space velocity $0.75 \text{ kgCH}_4 \text{ h}^{-1} \text{ kgcat}^{-1}$. Symbols are experimental data and lines are thermodynamic equilibrium predictions.

This preliminary experiment denoted that the sorbent and catalyst positively interact in this mixture and operating conditions used of $0.75 \text{ kgCH}_4 \cdot \text{h}^{-1} \text{ kg}^{-1} \text{ cat}$ and even at a very low Ni content of (around 1%) in the reaction bed. Despite this very low catalyst content our sorbent reached H_2 productions and CO_2 -carrying capacities that would fulfill the requirements described by Fernandez et al. 2012 [19] to sustain a Sorption Enhanced Steam Methane Reforming process at large scale. Our research group is currently working with this sorbent in order to study its performance at large scale SER operational conditions.

4. Conclusions

In this work, a series of synthetic CaO-based sorbents with a high CO_2 absorption capacity and chemically and mechanically stable during multi-cyclic operation (at least 40 calcination-carbonation cycles and 100 cycles in some cases) under the typical SER process conditions has been developed. Regarding the synthesis method and therefore

the nature of inert support (MgO or mayenite) it can be concluded that the co-precipitation method with the presence of MgO inert phase seems to favor the development of a rich structure with surface areas ranging from 16 m²/g to 26 m²/g, higher than that of natural CaO (12-15 m²/g) and high porosities ranging from 0.75 to 0.78. These materials presented a bimodal pore size distribution with an important pore volume in the range of pore diameters below 50 nm but, specially the material with lower CaO content, present also an important pore volume at higher pore diameters that could be associated with the presence of MgO. The XRD and SEM-EDX analysis confirmed the good distribution between Ca and Mg elements forming a uniform dispersion of small crystallites of CaO (32-40 nm) and MgO (16-23 nm). Thus, the finely-dispersed support among CaO particles would fully function as the metal matrix, which could effectively prevent the collapse of pore structure and further suppress the sintering of sorbent particles. On the other hand, sorbents prepared by mechanical mixing of calcined natural limestone and Ca aluminate cement presented a less surface area (7-10 m²/g) and porosity (0.55) with a mean pore diameter around 100 nm.

Regarding the sorption capacity and stability of both series of materials, the evolution of CO₂ carrying capacity of the materials with the number of reaction cycles has been evaluated using a TGA analyzer. It can be concluded that the sorbent performance is highly improved with respect to the material with no inert support and that a minimum amount of inert support is required to maintain sorbent activity (12.5 wt.% in the case of synthetic dolomites and a 10 wt.% in the case of CaO-Ca₁₂Al₁₄O₃₃ materials). The sintering resistance of the material with MgO inert support is higher and therefore its residual CO₂ carrying capacity after 100 cycles is notably better compared with the mayenite inert support one (0.29 and 0.20 gr_{CO2}/gr_{calcined sorbent} respectively).

Synthetic dolomites were subjected to a deeper performance analysis and it was concluded that whilst the amount of CaO might not affect the carbonation reaction kinetics, the conversion level at which the transition between reaction regimes take place is directly related with the amount of CaO present in the sorbent. The reactivity of particles formed by agglomeration has been also assessed. The results, as expected indicated that materials reactivity is reduced when increasing the particle size, and the CO₂ diffusion to the interior of the pore structure start to play a role for the bigger particle sizes. The joint performance of the best candidate material (CaO/MgO 2:1), and a commercial reforming catalyst has been tested under SER operation conditions. Despite the very low space velocity and low catalyst content used for this experiment, our sorbent reached H₂ productions and CO₂-carrying capacities that would fulfill the requirements to sustain a Sorption Enhanced Steam Methane Reforming process at large scale.

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