

SORPTION-ENHANCED STEAM REFORMING OF ETHANOL FOR HYDROGEN PRODUCTION

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Abstract— In last years, sorption-enhanced steam reforming of ethanol (SESRE) has become an interesting alternative for the industry, since it offers high H₂ purity with a simpler and smaller system. In this study CaO derived materials were synthesized to improve multicyclic CO₂ sorption-desorption stability. A dispersant and inert phase (Ca₁₂Al₁₄O₃₃) was incorporated into CaO structure. The effects of CaO:Ca₁₂Al₁₄O₃₃ ratio on the characteristics of the new adsorbents and on their performance in sorption-enhanced steam reforming of ethanol were analyzed. The results obtained indicate that the adsorbent 85% CaO – 15% Ca₁₂Al₁₄O₃₃ had significantly improved cyclic reaction stability. Additionally, it was proved that with this adsorbent CO purity on wet basis was lower than 2 %, making it possible to attain in only one reaction stage the CO purity obtained after de WGS reactor.

Keywords— CO₂ sorbent; Ethanol steam reforming; CaO; Mayenite

I. INTRODUCTION

Recently, H₂ has been proposed as a power vector, to substitute fossil fuels such as oil, coke, and natural gas, due to its beneficial environmental impact. An alternative to employ, H₂ as a power source is to feed it into a fuel cell, such as a PEM fuel cells, which requires high purity H₂ to be effective. Among many industrial processes for H₂ synthesis, the steam reforming of alcohols derived from biomass is a sustainable alternative. Thermodynamic studies have shown (Mas *et al.*, 2006) that the steam reforming of ethanol is feasible at temperatures greater than 773K, being the main products: CH₄, CO, CO₂ and H₂. Despite the apparent simplicity of the global reaction, the ethanol steam reforming (ESR) involves a complex system of reactions that affect the H₂ selectivity. In fact, the H₂ produced by this process contains significant amounts of CO, which poisons the anode at the PEM fuel cell (Lee *et al.*, 2008). To increase H₂ purity in the gaseous product containing additionally CH₄, CO₂, and CO, successive operational units are necessary to decrease specially CO concentration.

A well-studied strategy to purify the H₂ at the outlet of the reformer is to interpose before entering to fuel cell, a CO conversion reactor (WGS) that decreases the purity of CO up to 2% on wet basis followed by the reactor of

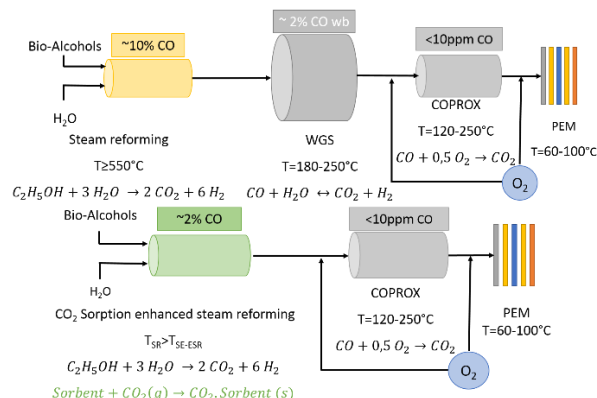
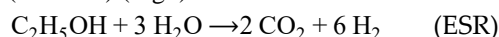


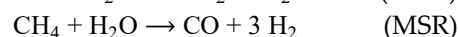
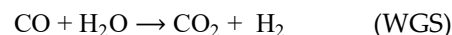
Figure 1. Scheme of the H₂ production as energy vector, by traditional ethanol steam reforming and CO₂ sorption enhanced ethanol steam reforming (SE-ESR).

CO partial oxidation, where the concentration of CO decreases to ppm (Fig.1).

Removing of CO₂ by sorption reaction with a sorbent might be an alternative to simplify the purification process (Comas *et al.*, 2004). The proposal is to replace the reformed by a single step process to integrate the reforming reaction and the selective separation of CO₂ by sorption, which is known as sorption-enhanced ethanol steam reforming (SE-ESR) (Fig 1).



The product distribution of ethanol steam reforming is determined by the equilibrium of the CO conversion (WGS) and methane steam reforming (MSR) reactions (Mas *et al.*, 2008 a,b; Grashinsky *et al.*, 2010). According to Le Chatelier's principle (Cunha *et al.*, 2013; Da Silva and Müller, 2011; Feng *et al.*, 2012; Wess *et al.*, 2015), in the presence of a CO₂ sorbent, such as CaO, the balance of the WGS reaction is modified during the reaction/separation process, increasing H₂ production and its purity.



CaO emerges as one of the most employed sorbents due to its good kinetics, high theoretical CO₂ capture capacity of 0.786 gCO₂/gCaO and low production costs (Erans *et al.*, 2016). The main drawback of CaO is the high temperature required for its regeneration (around 1073K) which leads to sintering and porous closure. As a consequence, a rapid decay of its sorption capacity is produced

throughout the multiple reaction and regeneration cycles (Lopez *et al.*, 2018). To improve CaO stability, the synthesis of CaO based materials has been proposed, which contain $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ as an inert phase that promotes CaO dispersion and avoid its sintering (Lopez *et al.*, 2018). The aim of the present study is to evaluate the performance and stability in sorption enhanced ethanol steam reforming (SE-ESR) of CaO based sorbents. For which solids with two different CaO- $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ ratios were synthesized and characterized.

II. MATERIALS AND METHODS

The synthesis method for the CaO derived sorbents was performed based on the one proposed by Li *et al.* (2005). CaO (Standar) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Biopack) were employed as precursors.

Both were added to the solution of 1 mol of 2-propanol and 5.8 mol of distilled water so that the weight ratios of CaO to newly formed materials ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$) would become 75/25 or 85/15 wt (%). The solution was stirred for 1 h at 353K. After drying all night in stove (393 K), the samples were calcined at 773 K for 3 h. Followed by a two steps treatment of the samples; first, water was added and the obtained kneaded paste was dried overnight at 393 K; finally, the resulting solid was calcined at 1173 K for 1.5h. For drying or calcination step, the employed temperature ramp was 10 K/min. The samples were named D75 and D85 respectively. Pure CaO was also prepared by the calcination of high-purity CaCO_3 (Biopack 99,0%) at 1173 K and 1 atm for 8 hours. Complete CaCO_3 conversion was confirmed considering that 0.56 g of CaO are formed per gram of original CaCO_3 . Solid characterization was carried out by different techniques: the crystalline structure of the sorbents was characterized by X-ray diffraction (XRD) on a Siemens D500 diffractometer using Cu Ka radiation ($\lambda = 1.5406\text{\AA}$). Specific surface area and pore size distribution were measured on a Quantachrome Autosorb automated gas sorption system. The measurements were performed using nitrogen physisorption and desorption isotherms at 77K. The sorbents were degassed at 523K overnight in the degassing port before the actual measurements. BJH method was applied for the determination of pore size distribution. The microstructure of samples was analyzed by scanning electron microscopy (SEM), model Zeiss NTS – SUPRA 40, 50KX. The sorption capacity ($C_s(t)$) of the samples, defined in Eq. 1 was determined in a Thermobalance Q600.

$$C_s(t) = \frac{m_{\text{CO}_2}^{\text{abs}}(t)}{m^0 w_{\text{CaO}}} \quad (1)$$

where $m_{\text{CO}_2}^{\text{abs}}(t)$ (g) is the amount of CO_2 absorbed at certain time, t (min); m^0 (g) is the initial mass of sorbent before reaction, and w_{CaO} is the content of CaO in the initial mass of sorbent.

The CO_2 sorption capacity tests were carried out in the thermobalance under the following conditions: 200 mL/min of CO_2 (15%) in N_2 , initial sorbent mass of 20 mg, particle size between 177-297 μm and sorption temperature 823 K. In each run the implemented protocol

was the following: the sample, previously weighed, was exposed to an increasing temperature with a ramp of 10K/min from ambient temperature to 873 K, under N_2 stream. Once reached, this temperature was kept for 30 min to reverse the possible formation of $\text{Ca}(\text{OH})_2$. Then, cooling to 273 K was carried out followed by heating at 10 K/min up to 1123 K, this temperature was maintained for 20 minutes, to ensure that all the $\text{Ca}(\text{CO}_3)_2$ formed was decomposed to CaO. Subsequently, the sample was cooled to the reaction temperature (823 K) and the feed composition was changed to 15% CO_2 in N_2 , maintaining this temperature for 15 minutes.

Stability of CO_2 sorption tests (without reforming reaction) were performed in a Micromeritics AutoChem II over CO_2 sorption-desorption cycles. CO_2 sorption was made during 15 min at 823 K in a 15% CO_2 - N_2 stream; desorption took place at 1123 K for 5 min under inert atmosphere. Cyclic stability is defined as:

$$C_s(n) = \frac{m_{\text{CO}_2}(n)}{m_{\text{max,CO}_2\text{abs}}} \quad (\text{g/g}) \quad (2)$$

where n : cycle number; $m_{\text{CO}_2}(n)$: mass of absorbed CO_2 in cycle n , $m_{\text{max,CO}_2\text{abs}}$: mass of absorbed CO_2 in the first cycle.

SE-ESR tests were carried out in a fixed-bed reactor. The catalyst used was a Ni-Mg-Al catalyst previously synthesized by our group (Romero *et al.*, 2010). Catalyst precursors were prepared by homogeneous precipitation method based on urea hydrolysis, for which solutions containing urea-Ni(II)-Mg(II)-Al(III) in proper ratios for each catalyst; were aged at 363 K during 24 h in PP bottles. The reaction was quenched submitting the bottles into ice-bath. The precipitated precursors were centrifuged, washed with cold distilled water and dried at 343 K. Total concentrations for the starting solutions of urea and cations $[\text{Ni}(\text{II}) + \text{Mg}(\text{II}) + \text{Al}(\text{III})]$ were 0.5 mol/L and 5.0×10^{-2} mol/L, respectively. Initial molar ratio of $[\text{Ni}(\text{II}) + \text{Mg}(\text{II})]/\text{Al}(\text{III})$ were 2 and $\text{Mg}(\text{II})/\text{Ni}(\text{II})$ ratio was 1 (Romero *et al.*, 2014). The reactor packing consisted in a homogeneous mixture of 620 mg of catalyst and 880 mg of sorbent. It had been proved previously that this configuration had the best catalytic performance with CaO as sorbent (Menendez *et al.*, 2018). The reactants, a mixture of water and ethanol, were fed in liquid state by a syringe type pump. The mixture was evaporated in an electric oven at 573K and afterwards diluted with an argon/nitrogen stream (N_2 : Ar: $\text{C}_2\text{H}_5\text{OH}$: H_2O =0.178:0.708:0.017:0.095). Feed and out streams were analyzed by gas chromatograph; with TCD and FID detectors. The reaction was carried out at 823 K, with water: ethanol molar ratio of 5.5 for 5 min. Regeneration process was performed at 1123 K during 10 min under N_2 stream.

The ethanol steam reforming was also performed under the same conditions, catalysts loading and without CaO based sorbent. Total conversion of ethanol was obtained and the typical product distribution for the steam reforming was observed (Menendez *et al.*, 2018). Therefore, based on this result, it is possible to ensure that complete ethanol conversion was achieved under the reaction

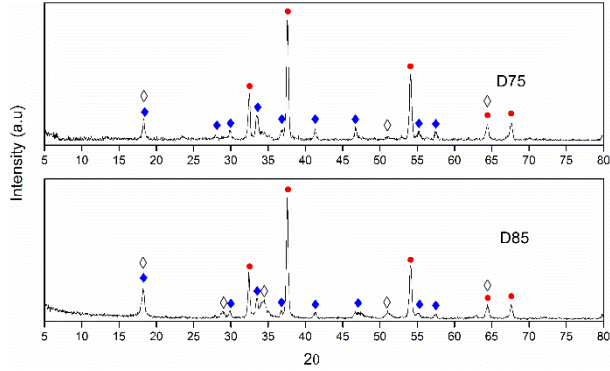


Figure 2. XRD pattern of the synthesized $\text{CaO-Ca}_{12}\text{Al}_{14}\text{O}_{33}$ D75 and D85 fresh samples. \blacklozenge $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (JCPDS: 060413 0.064); \bullet CaO (JCPDS: 37497 0.083); \diamond Ca(OH)_2 (JCPDS: 040733 0.205).

conditions in the cyclic stability tests. Additionally, the purities of H_2 , CO_2 and CO on dry basis for ethanol steam reforming were 72.6%, 17.1% and 9.5 %, respectively. H_2 and CO purity were expressed in dry basis, as seen in Eq. 3.

$$P_j = \frac{y_j}{1 - y_{Ar} - y_{N_2} - y_{H_2O}} \quad (3)$$

where y_j : molar fraction of j product at reactor outlet. y_{N_2} and y_{Ar} molar fraction of inert and y_{H_2O} water molar fraction

To compare the results with those obtained in the WGS, the purity on wet base were also determined (Eq. 4):

$$P_j = \frac{y_j}{1 - y_{Ar} - y_{N_2}} \quad (4)$$

III. RESULTS AND DISCUSSION

In Fig. 2, the diffractograms corresponding to the synthesized solids, derived from CaO , are presented. For both samples, it is possible to distinguish the presence of 3 phases. First, a minor phase of Ca(OH)_2 , which can be related to its incomplete decomposition during calcination (Martavaltzi and Lemonidou, 2008). The CaO phase was also identified, its peaks of greater intensity in each solid indicate that this crystalline phase was in greater proportion, besides being more intense in the sample with a higher nominal content of CaO . Finally, the presence of the desired dispersant phase, of molecular formula $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, named mayenite was also distinguished.

Scanning electron microscopy of the fresh samples CaO , D75 and D85 are shown in Fig. 3. The micrograph corresponding to fresh CaO , showed the presences of agglomerates of CaO phase. Conversely, the micrographs corresponding to D85 and D75 confirmed the formation of the dispersant and inert phase, $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, and the presence of small agglomerates of CaO phase. Therefore, $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ phase favors the conformation of a microstructure finely dispersed, for D85 and D75 absorbents.

Figure 4 shows the results of CO_2 sorption capacity obtained in the thermobalance equipment in one step of carbonation with fresh solids. D85 showed the best performance, while D75 sorbent presented the lowest absorption capacity. Based on this result it is possible to

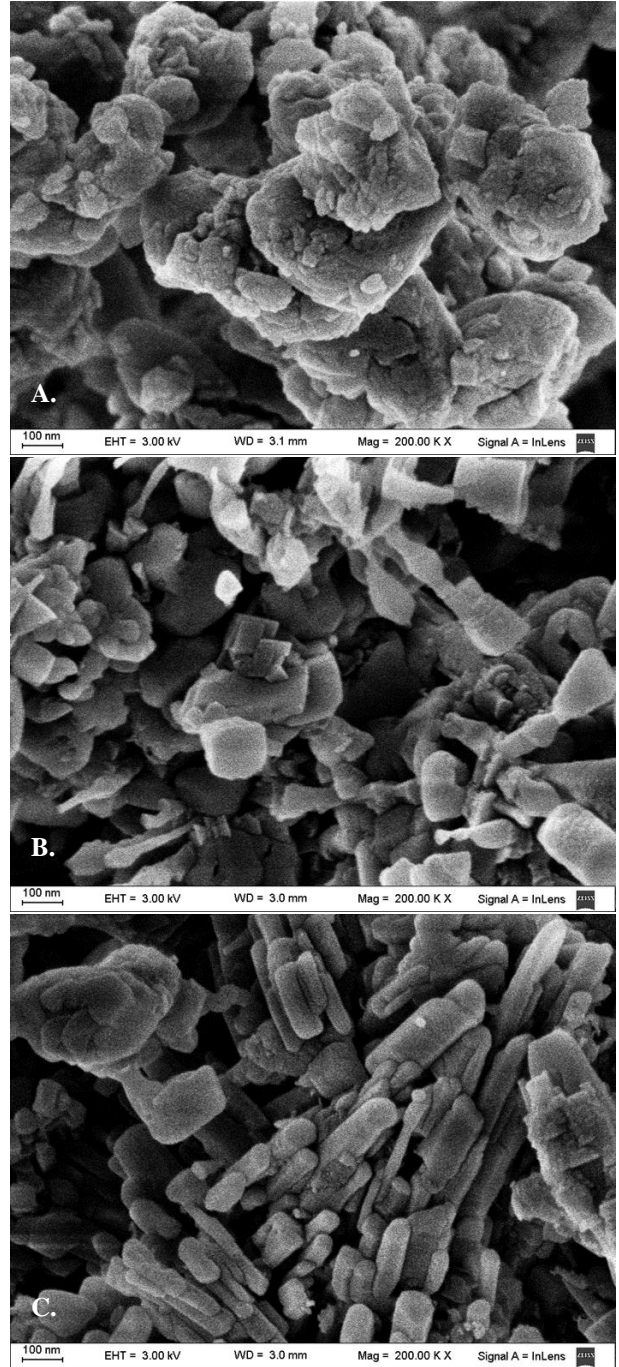


Figure 3. SEM images of fresh samples: A) CaO ; B) D75; C) D85.

postulate that there is an optimum ratio $\text{CaO}:\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, which enhanced sorbent capacity per gram of CaO . At lower ratios, the presence of higher contents of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ might obstruct the pathway to the active CaO sites.

With the increasing carbonation/calcination cycles, structural changes in the sorbent particle takes place, as sintering of CaO phases during calcination cycles. The effect of the inert phase on CaO sintering is analyzed by stability tests. These tests were performed in a Micromeritics AutoChem II over CO_2 sorption-desorption cycles for the different samples, as is shown in Fig. 5.

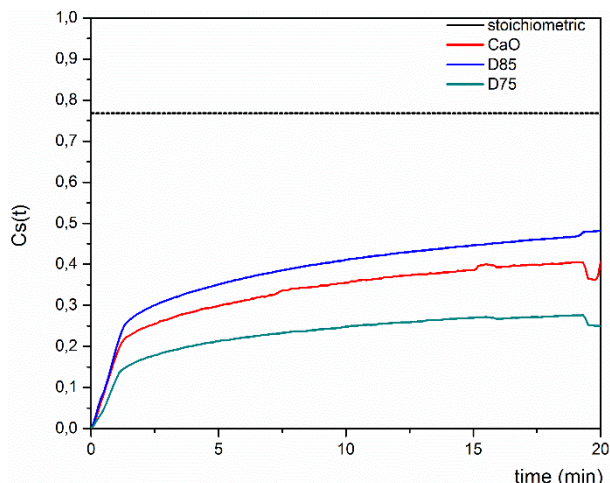


Figure 4: Sorption capacity of synthesized solids and CaO, at one sorption stage (sorption: 550 °C, 20 min, 15% v/v CO₂). Comparison with maximum (theoric) values.

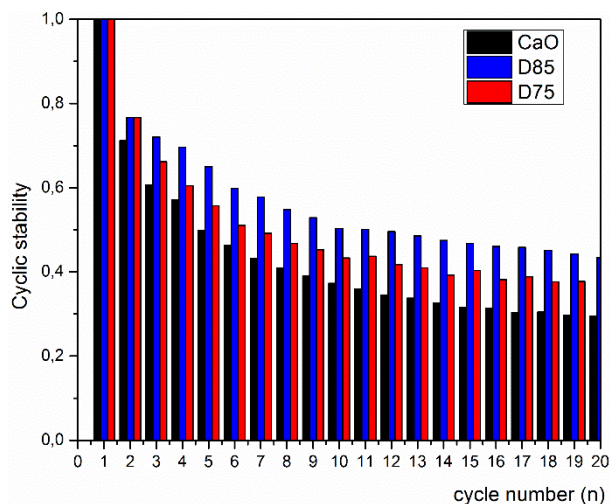


Figure 5. Cyclic stability of the solids during 20 cycles of sorption-desorption (sorption:550°C, 30 min, 15% v/v CO₂; desorption: 850 °C, 10 min, 100% Ar).

The D85 solid presented the best performance, showing the highest stability for 20 cycles. Conversely, CaO showed the most unfavorable results, since its sorption capacity rapidly decreased by almost 70% for the last cycles. Abanades and Alvarez (2003) attributed the decay of CaO conversion to a loss of small pore and an increase of large pores; since when small CaO particles are heated, CaO coalesces, sinters and its surface and porosity decrease.

In Table 1 the textural properties of the solids, fresh and used after 20 cycles of reaction and subsequent regeneration, are shown. It is observed, for the used samples D75 and D85, after 20 cycles of carbonation and regeneration, that the specific surface area does not change, and the average pore radius increases due to the formation of larger pores. Li *et al.* (2005) have reported that particle growing has not been found when analyzing the microgranular appearance of particles after a large number of cycles of carbonation – regeneration for CaO/Ca₁₂Al₁₄O₃₃ sorbents, unlike the effect informed for

Table1. Textural properties of the fresh solids: CaO, D75 and D85; and textural properties of the sorbents after 20 cycles and regeneration.

Sorbents	BET area (m ² /g)	Poral volume (cm ³ /g)	Pore radius (Å)
Fresh samples			
CaO	68.3	0.17	30.8
D75	44.7	0.13	40.7
D85	42.5	0.13	40.4
Samples after 20 cycles and regeneration			
CaO	51.3	0.15	77.5
D75	49.7	0.15	75.4
D85	41.9	0.17	70.3

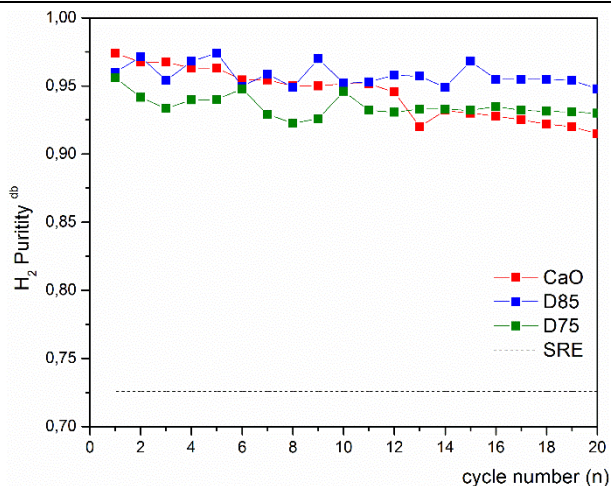


Figure 6. H₂ purity on dry basis in SE-SRE with CaO and synthesized sorbents.

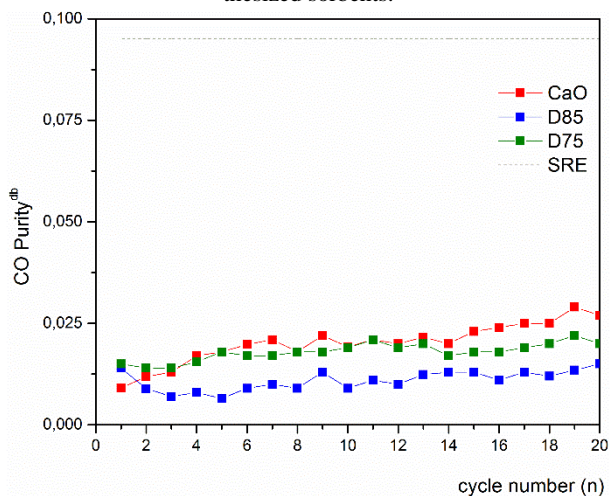


Figure 7. CO purity, on dry basis, in SE-SRE with CaO and synthesized sorbents.

CaO sorbent by Abanades and Alvarez (2003). This confirms that Ca₁₂Al₁₄O₃₃ produces textural changes preventing the sintering of CaO phase.

Figure 6 and 7 shows the purity results of H₂ and CO, on dry basis, as a function of the number of reaction-sorption and regeneration cycles in the SESRE process. H₂ purity was significantly improved by the presence of a sorbent in comparison with traditional ethanol steam reforming which is around 0.73 (Menendez *et al.*, 2018). Regarding CO purity it is evident a substantial decrease compared to ESR. While CO₂ purity on dry basis is lower

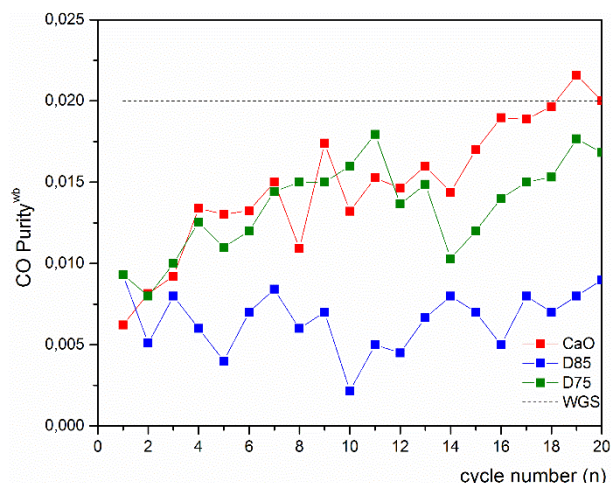


Figure 8. CO purity, on wet basis, in SE-SRE with CaO and synthesized sorbents.

than 4% for each cycle (not shown). Additionally, in Figure 8, CO purity on wet basis is shown, being this purity lower than 2% for D-85, for the whole 20 cycles.

Therefore, it is demonstrated that CO concentration at the exit of the SE-ESR is like that the one obtained at the output of the WGS reactor. Therefore, it is possible to simplify the number of purification stages in order to obtain lower CO content at the feed of fuel cell.

By the images of SEM of used solids (Fig. 9) it is evident, after 20 cycles of reaction and regeneration, the formation of conglomerates of CaO particles for CaO pure, but such formations is not observed in CaO/Ca₁₂Al₁₄O₃₃ samples.

IV. CONCLUSIONS

It was proved that the sorbent with the optimum performance in the cyclic process of sorption enhanced steam reforming of ethanol and regeneration was CaO/Ca₁₂Al₁₄O₃₃ (85/15). This solid possesses the adequate proportion of absorbent (CaO) and dispersant (Ca₁₂Al₁₄O₃₃), giving the system greater stability and absorption capacity. This ratio allows a stable behavior with a good absorption capacity.

Although other authors have promoted the advantage of the Ca₁₂Al₁₄O₃₃ phase modifying the CaO, the studies were limited to the analysis of the sorption - regeneration without its application to the ethanol steam reforming reaction.

In this work we have shown that it is feasible to obtain higher H₂ purity and stability for 20 cycles of reaction/sorption and regeneration, as a minimum, with concentrations of CO lower than 2%, on wet basis, at the exit of sorption-enhanced ethanol steam reforming unit using an homogeneous mixture of catalyst and sorbent, similar to the one obtained in the traditional purification system in the exit of WGS reactor.

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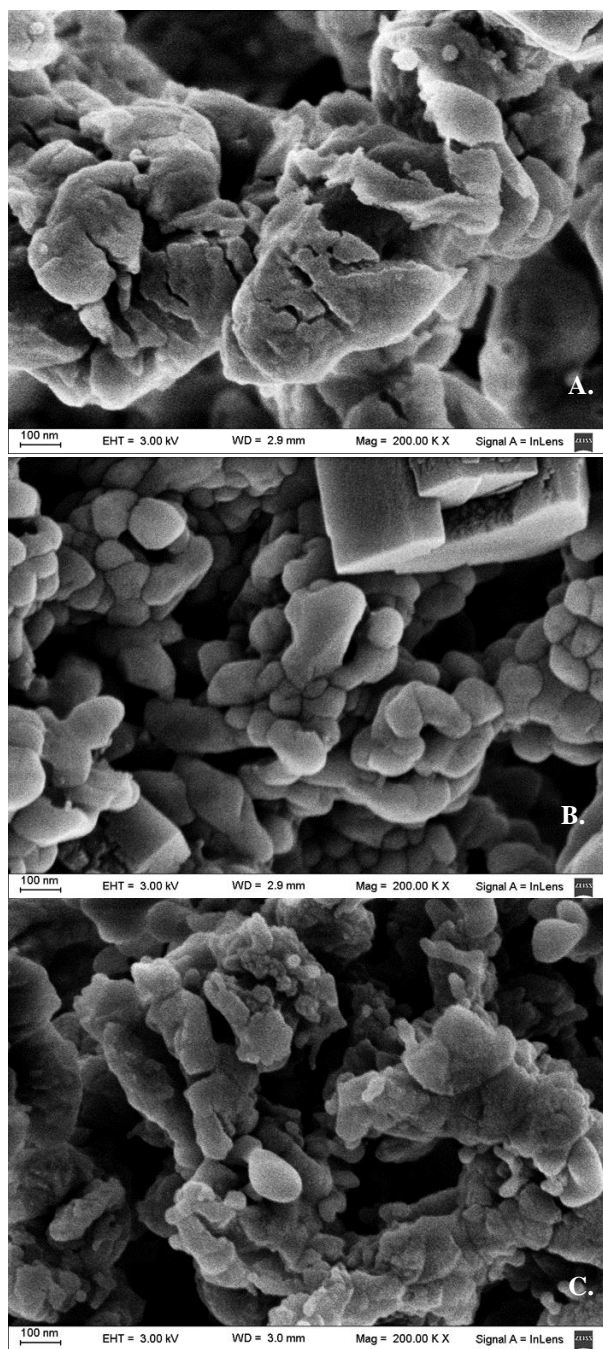


Figure 9: SEM images of used samples: A) CaO; B) D75; C) D85.

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