Sorption-Enhanced Ethanol Steam Reforming Process in a Fixed-Bed Reactor

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ABSTRACT: Sorption-enhanced ethanol steam reforming is an alternative to nonrenewable sources to produce high purity hydrogen by simplifying the purification train required to obtain cell grade hydrogen. In this work, NiMgAl hydrotalcite was used as a catalyst precursor and CaO as a sorbent. The catalyst–sorbent configuration in the fixed-bed reactor, the effect of the sorbent/ catalyst mass ratio, and the reaction temperature were the focus of our study. It was found that the well-mixed catalyst and sorbent configuration resulted in the highest hydrogen purity in the prebreakthrough period and the lowest CO concentration. Besides, it was possible to produce high purity hydrogen (>95%) at 723 K with a hydrogen yield equal to that obtained at 873 K without

sorbent. Finally, it was corroborated that after 20 reaction/regeneration cycles the CO concentration was still lower than that obtained at the WGS reactor exit.
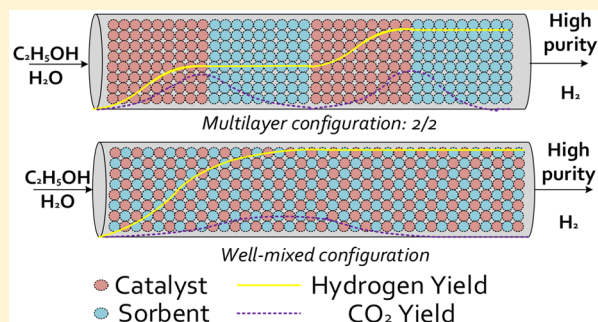
1. INTRODUCTION

The concept of a hydrogen economy,[1] in which this energy carrier is considered to have the potential to replace fossil fuels, has generated numerous research studies.[2−4] In this scenario, hydrogen is presented as an environmentally sustainable alternative to produce energy, and among its many applications, the generation of electricity through the use of fuel cells is very promising. To generate zero CO_2 emissions, hydrogen must be produced from renewable raw materials such as bioethanol, glycerol, or bio-oil through a steam reforming process.

The ethanol steam reforming (ESR) is one of the most studied reaction for the production of hydrogen. Catalysts based on Ni have demonstrated good selectivity to hydrogen and are less expensive than that based in noble metals. However, it is known that Ni catalysts can be deactivated by a process of sintering. The metal–support interaction plays an important role during the impregnation step and thermal treatments, since both of them can define the properties of final catalysts: reducibility, resistance to thermal sintering of the active sites, or metallic dispersion.[5] In this sense, Ni/Al_2O_3 catalysts obtained from lamellar double hydroxides (LDHs) as precursors have been shown to be a promissory alternative, since Ni(II)−Al(III) LDH compounds present, after reduction treatment, Ni metal particles highly dispersed in an aluminum structure.[6] Particularly, Mg(II)Ni(II)Al(III) catalysts prepared from LDH precursors exhibit high activity and, most important, good long-term stability for ethanol steam reforming.[7] The results obtained showed that the Mg addition to the Ni(II)Al(III) precursor leads to catalysts exhibiting higher activity than those without Mg, with an important reduction in the amount of deposited coke, due to inhibition of

ethanol dehydration toward ethylene. Moreover, in a previous work, Romero et al.[8] concluded that thermal treatments of Ni(II)Mg(II)Al(III) LDHs lead to synergetic effects between the elements in mixed oxides structures, and after appropriate activation treatment, give rise to well dispersed metal particles like a supported metal catalyst, with the possibility of controlling metal−support interaction during the synthesis and treatment stages.

Thermodynamic studies have shown[9] that the ESR is feasible at temperatures greater than 773 K, the main products being CH_4, CO, CO_2, and H_2. But, the H_2 produced by this process contains significant amounts of CO, which poisons the anode at the fuel cell.[10] Different technologies have been developed in order to obtain ultrapure H_2 (<10 ppm of CO) among which it is possible to mention water gas shift (WGS) reactor followed by preferential oxidation of CO (COP-ROX),[11,12] or diffusion of H_2 through membranes.[13,14] Removing CO_2 by an adsorption reaction with a sorbent might be an alternative to overcome this drawback. A single-step process to integrate the reforming reaction and the selective separation of CO_2 by sorption has been proposed, which is known as sorption-enhanced ethanol steam reforming (SE-ESR).[15,16]

Since the ethanol steam reforming products distribution is limited by the equilibrium of the CO conversion WGS and methane steam reforming (MSR) reactions,[17−19] according to Le Chatelier's principle,[20−24] the balance of the WGS reaction
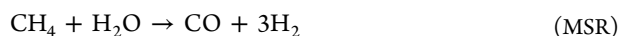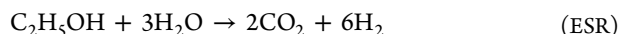
changes during the reaction/separation process, increasing the H_2 production and its purity. An additional advantage of the SE-ESR process is that the heat generated in the adsorption reaction offsets the heat required for the steam reforming to occur; for example, the adsorption heat for the CaO carbonation (SE) is −176 kJ/mol and the reaction heat of ESR is +174 kJ/mol. However, since the behavior of the sorbent in the reaction makes the regeneration necessary, more energy is required in the global/cyclic process.

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \qquad \text{(ESR)}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \text{(WGS)}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \text{(MSR)}$$

$$CaO + CO_2 \rightarrow CaCO_3 \qquad \text{(SE)}$$

Within the past few years, the concept of combining reaction and separation to simplify chemical processes and to improve product purity has achieved special attention.[21,25−27] The key to the success of the process is the selection of a suitable sorbent operating at high temperatures (>673 K). Different sorbents were reported in the literature as potential candidates, for example, mixed oxide materials such as calcium oxide and lithium metal oxides such as lithium zirconate and lithium orthosilicate. These materials are suitable for this type of reaction, because they capture CO_2 between 723 K and 1023 K and, above this temperature, they can release it reversibly by a calcination reaction.[27] CaO-based sorbents are advantageous due to their high CO_2 sorption capacity and high rate of sorption in a wide range of temperatures and pressures, besides their low cost and availability.[28−30]

Many published studies about the design of the reforming reactor with CO_2 sorption employ fixed-bed reactors filled with sorbent and catalyst.[21,31,32] Rawadieh and Gomes[33] have carried out the simulation study on sorption-enhanced steam methane reforming process with different layered systems (catalyst/absorber in 1/1, 2/2, and 4/4 layers) and another well-mixed catalyst/sorbent configuration for comparison. They found that the adsorptive reactor with well-mixed catalyst/sorbent materials produce high purity hydrogen with a low CO content.

The LDH (NiMgAl) catalyst precursor was developed by our group for the ESR reaction.[8] Different Mg(II)/Ni(II) molar ratios were tested, and it was found that the catalyst with the better performance is that with a ratio equal to 4.[34] With this solid 5.2 mol of hydrogen per mol of ethanol in the feed was obtained. Because of this result, the aim of this paper is to analyze the ethanol steam reforming reaction with simultaneous CO_2 sorption employing CaO as sorbent and the previous developed catalyst. The effect of different configurations, sorbent/catalyst ratios, and temperature are studied. Continuous operating cycles are performed in order to obtain high purity hydrogen under stationary conditions.

2. EXPERIMENTAL SECTION

The nitrogen adsorption−desorption technique (Micromeritics ASAP 2020) was used to find the Brunauer−Emmet−Teller (BET) surface area, pore volume, and average diameter pore for the CaO sample. Micromeritics AutoChem II equipment coupled to mass spectrometer Thermostar Pfeiffer was used for the carbonation and regeneration experiments in order to evaluate the stability of pure CaO during 20 cycles. Sorption was carried out with a 15% CO_2 in Ar stream for 15 min at 823 K. Low CO_2 pressure was used to simulate the real composition of the reformer exit. Desorption was implemented under pure Ar (20 mL/min) through a ramp of 10 K/min from 823 K to 1123 K and remaining there for 5 min. The cyclic stability of the sorbent, $Cs(n)$, was defined as the ratio between the CO_2 mass sorbed in cycle n and the maximum sorption capacity of the solid.

The catalytic evaluation was performed in a stainless steel reactor of 12.5 mm internal diameter and 240 mm long located in an electric oven. Reaction temperature was controlled by a thermocouple placed inside the catalytic bed. 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 573 K and afterward diluted with an argon/nitrogen stream (160 mL/min of Ar and 40 mL/min of N_2). Preliminary tests allowed a demonstration of the absence of external limitations. The catalyst was ground to an average diameter of 237 μm, and it was found that, for that particle size, diffusional limitation in the interior of the particle was negligible.[35] The isothermicity was maintained due to the high reactants dilution. The minimum bed length was about 35 mm so the ideal plug flow reactor hypotheses were fulfilled. The liquid flow was fixed in 1.7 mL/h, and the water−ethanol molar ratio (R) was 5.5. The total molar fraction of ethanol and water was 0.02 and 0.11, respectively. For these operating conditions the spatial time was 3.4 $g_{cat} \times$ min/mmol$_{ethanol}$. The feed and effluent pipes were heated to avoid any condensation. Stainless steel pipes were used to prevent ethanol decomposition out of the catalytic bed.

The reactor packing consisted of LDH NiMgAl reforming catalyst, which was previously developed and characterized with high activity in ethanol steam reforming,[8,34,36] and CaO obtained by calcining high-purity $CaCO_3$ (Biopack 99,0%) at 1123 K and 1 atm for 8 h. Complete $CaCO_3$ conversion was confirmed taking into account that 0.56 g of CaO are formed per gram of original $CaCO_3$. The average particle size of CaO was 237 μm. LDH NiMgAl catalyst was activated in situ by direct reduction in a hydrogen stream at 973 K for 1 h. The temperature ramp rate was programmed at 10 K/min to reach the activation temperature. During cyclic experiments, the regeneration of the CaO was carried out in a N_2 stream (50 mL/min) from the reaction temperature to 1123 K through a ramp of 10 K/min and is maintained for 10 min at this temperature before returning to the reaction temperature to continue the next cycle. Two blank runs were also performed, the first one with only inert material and the other with only CaO. In both cases the ethanol conversion was negligible.

The catalyst-sorbent configurations used were (i) 1/1, two layers, 1 layer of catalyst (m_{cat} = 620 mg) and 1 layer of CaO (m_{CaO} = 880 mg); (ii) 2/2, four layers, two layers of catalyst (310 mg each) and two layers of sorbent (440 mg each) intercalated, and (iii) well-mixed; in this case 620 mg of catalyst was mixed with 880 mg of CaO. To determine the products distribution obtained under ethanol steam reforming conditions, the reaction was carried out with 620 mg of catalyst and inert material (880 mg) of the same diameter (237 μm).

Inlet and product streams were analyzed by a gas chromatograph using argon as carrier gas, equipped with two capillary columns, Supelco Carboxen 1010 plot, used to separate gases, and HP-Innowax, for liquids, and two detectors: TCD and FID. The reaction temperature was fixed at 823 K for runs in which the temperature effect was not studied.

The analysis of the results was carried out according to the parameters defined in Table 1.

Table 1. Parameters for Analysis of the Results[a]

ethanol conversion	$X_{et} = \dfrac{F_{et}^0 - F_{et}}{F_{et}^0}$
hydrogen yield	$Y_{H_2} = \dfrac{F_{H_2}}{F_{et}^0}$
CO, CO$_2$, and CH$_4$ yields	$Y_i = \dfrac{F_i}{2F_{et}^0}$
molar fraction wet basis	$y_i^{wb} = \dfrac{y_i}{(1 - y_{Ar} - y_{N_2})}$
molar fraction dry basis (purity)	$y_i^{db} = \dfrac{y_i}{(1 - y_{Ar} - y_{N_2} - y_{et} - y_{H_2O})}$

[a]Definition of parameters: F_i^0, inlet molar flow component i; F_i, outlet molar flow component i; y_i, total mole fraction.

3. RESULTS AND DISCUSSION

3.1. CaO Characterization. A decay in CaO sorption capacity is observed as it is subjected to repeated cycles of sorption−regeneration (Figure 1). It can be seen that the CaO
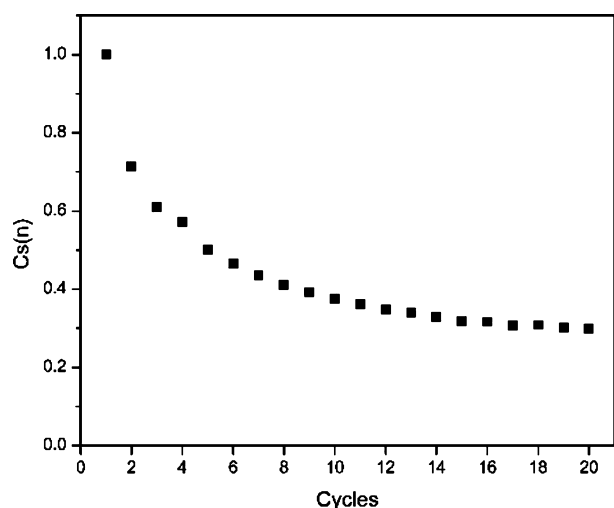

Figure 1. Cyclic stability of CaO.

sorption capacity decreases until it remains constant from cycle 14 at 32% of maximum capacity. This result is in line with those achieved by Abanades et al.[37] The sorption capacity decays due to the lack of useful porosity since the carbonation conversion depends on the fraction of porosity associated with micropores (less than 100 Å). As these authors demonstrated, during every calcination stage, the CaO micrograins undergo a sintering process, which leads to their clustering with the reduction in the microporosity. They also demonstrated an increase of mesoporosity due to CaCO$_3$ recrystallization, which leads large pores.[38]

Results in Table 2 are consistent with the proposed mechanism; the decrease in the specific area is a consequence of the microporosity decrease.

3.2. Reaction Tests. The SE-ESR tests were carried out using 620 mg of catalyst and 880 mg of CaO arranged in the different configurations described above: 1/1, 2/2, and well-

Table 2. Surface area, Pore Volume and Average Pore Radius for Fresh and Regenerated CaO

(cycles)	BET area (m^2/g)	radius (Å)	volume (cm^3/g)
CaO (0)	61.9	74.6	0.23
CaO (20)	2.7	479.6	0.02

mixed. The typical evolution of CO$_2$ concentration during the SE-ESR is shown in Figure 2, for the well-mixed configuration.
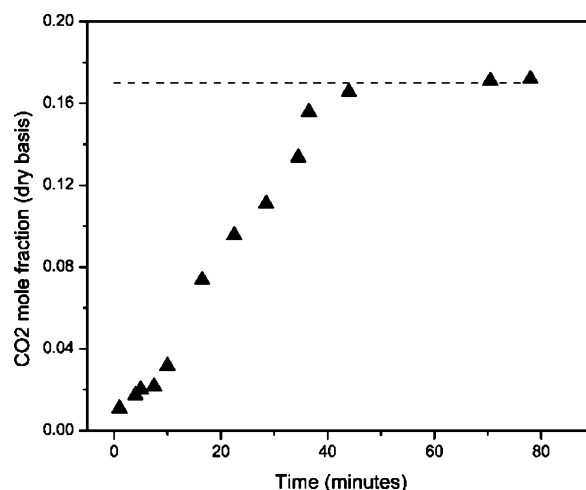

Figure 2. y_{CO2}^{db} for well-mixed catalyst/sorbent configuration: m_{cat} = 620 mg; m_{CaO} = 880 mg; reaction temperature = 823 K; R = 5.5. (▲) well-mixed; (dash line) ESR.

Three periods are identified: (1) prebreakthrough (Pre-B) period, in which the CO$_2$ concentration is low or null, indicating that the reforming and CO$_2$ separation reactions occur at maximum efficiency; most of the CO$_2$ produced from WGS reaction was effectively captured; (2) breakthrough (B) period, where the CO$_2$ concentration increases indicating the sorption enhanced effect weakens due to the diffusion limitation through the CaCO$_3$ layer that forms around the unreacted CaO core;[39] (3) postbreakthrough (Post-B) period, in which the CaO is saturated and the catalyst behaves like the conventional ESR reaction (y_{CO2}^{db} = 0.17).

As it can be concluded from Figure 3, the homogeneous mixture is the one that allows obtaining the highest purity of H$_2$ followed by the multilayer configuration 2/2. For all configurations, the molar fraction of H$_2$ in dry base decreases as CaO saturates, reaching in Post-B the purity of H$_2$ corresponding to the ESR (y_{H2}^{db} = 0.73).

The 1/1 configuration has a behavior equivalent to two processes in series: reaction in the catalyst layer followed by CO$_2$ sorption in the CaO layer. In the catalytic bed, the reforming reaction occurs generating a gaseous mixture with the typical ESR products distribution. In the CaO layer, only CO$_2$ sorption occurs. Thus, in this configuration, there is no equilibrium displacement, and the improvement in the H$_2$ purity is linked to the purification process of the reformed exhaust stream. The 2/2 configuration exhibits the same behavior in the first two layers: the CaO purifies the output current of the catalytic bed that precedes it. In the second catalyst layer, as there is no ethanol since it is completely consumed in the first stage (total conversion of the reformer), the WGS and SMR reaction proceed from CO, H$_2$, CH$_4$, and CO$_2$, the latter being eliminated in the second CaO layer. So,
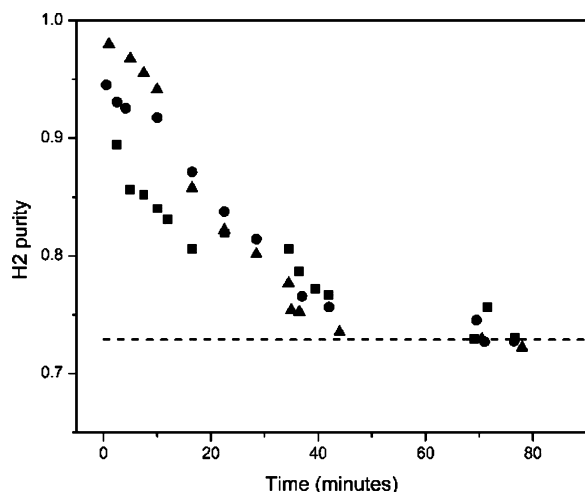
Figure 3. y_{H2}^{db} for different catalyst/sorbent configuration: m_{cat} = 620 mg; m_{CaO} = 880 mg; reaction temperature = 823 K; R = 5.5. (■) 1/1; (●) 2/2; (▲) well-mixed; (dash line) ESR.

as the number of layers increases, the interaction between reaction and sorption increases, and therefore, a better performance of the system is obtained. The homogeneous mixture configuration represents a limiting case since it can be understood as infinite layers of catalyst and sorbent.

Another aspect to be highlighted is shown in Figure 4, where it can be seen that the molar fraction of CO at the end of the
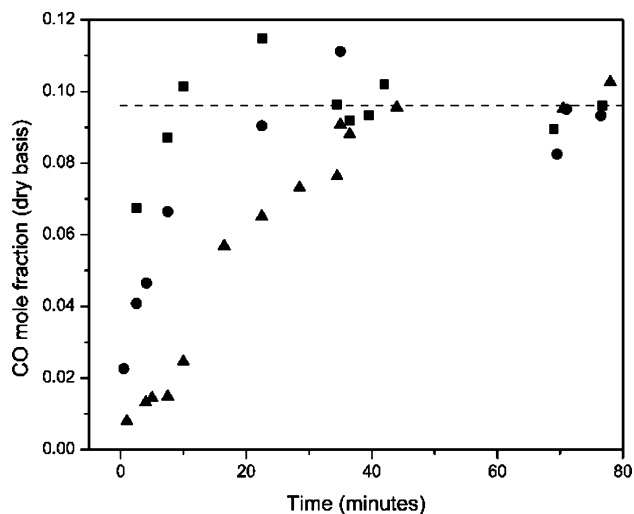

Figure 4. y_{CO}^{db} for different catalyst/sorbent configuration: m_{cat} = 620 mg; m_{CaO} = 880 mg; reaction temperature = 823 K; R = 5.5; (■) 1/1; (●) 2/2; (▲) well-mixed; (dash line) ESR.

breakthrough period for the multilayer configurations is higher than that of the ESR. This is due to the concentrating effect exerted by the CO_2 sorption. Once the CaO is saturated, the compositions tend to the steady-state value of the ESR. These results agree with the simulation work of Rawadieh et al.[33]

In the well-mixed configuration the Post-B period is reached more quickly than for the 1/1 configuration. This behavior could be explained by the increase in the number of layers making the interaction between reaction and sorption more efficient, causing a faster sorbent saturation. This result was also found in the theoretical study of Rawadieh et al.[33]

The effect of the sorbent/catalyst mass ratio was analyzed using the well-mixed configuration. The following sorbent-catalyst mass ratios were tested: 0.8, 1, 1.4 and 2; always using 620 mg of catalyst and operating at reaction temperature of 823 K.

It was demonstrated that the greater is the mass of CaO, the lower is the CO_2 content in the product stream during transient period B, and the greater the duration of this period is (Figure 5). That is, when the sorbent/catalyst mass ratio is
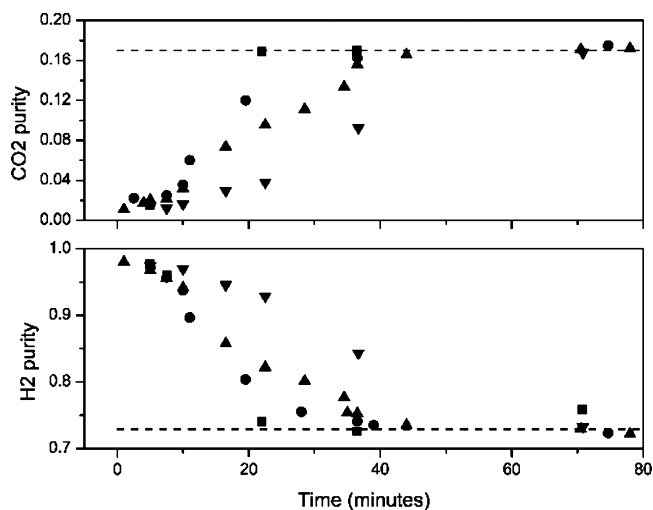

Figure 5. (a) CO_2 purity (b) H_2 purity for different sorbent/catalyst mass ratios. m_{cat} = 620 mg; reaction temperature = 823 K; R = 5.5; well-mixed configuration; (■) 0.8; (●) 1.0; (▲) 1.4; (▼) 2.0; (dash line) ESR.

increased, there is a greater amount of solid where CO_2 can be sorbed, and therefore it will take longer to become saturated. In contrast, during the period Pre-B there were no significant changes in the concentrations of the products as the CaO mass increased. However, Cunha et al.[32] using Ni/Al_2O_3 as a catalyst and a HTlc type sorbent in a layered arrangement obtained an improvement in H_2 purity by increasing the ratio from 0.6225 to 15, going from 62% to a value close to 100% in the period Pre-B. This suggests that, in order to obtain appreciable changes in the results, a considerable increase in the ratio is necessary.

One advantage of this process, in which reforming and sorption coexist, is that the heat generated during the CO_2 sorption compensates the heat required by the reforming. To study this effect, the reaction was carried out at 673, 723, 773, 823, and 873 K for the well-mixed configuration of 620 mg of catalyst and 880 mg of sorbent.

The hydrogen purity obtained in the period Pre-B is higher than that in the period Post-B over the entire temperature range studied here (Figure 6). It is remarkable that between 723 and 823 K, the variation in H_2 purity in the period Pre-B is negligible, due to the exothermicity of the adsorption reaction that allows the reforming reaction to occur at a lower temperature. This result indicates that it is possible to obtain a product of the same quality in a wide range of temperatures, which is relevant for industrial applications, for which isothermal conditions are difficult to maintain. At 873 K, however, a sharp decrease in the H_2 purity with respect to that at 823 K is observed. This is due to the decrease of the sorption capacity of the CaO when increasing the temperature.
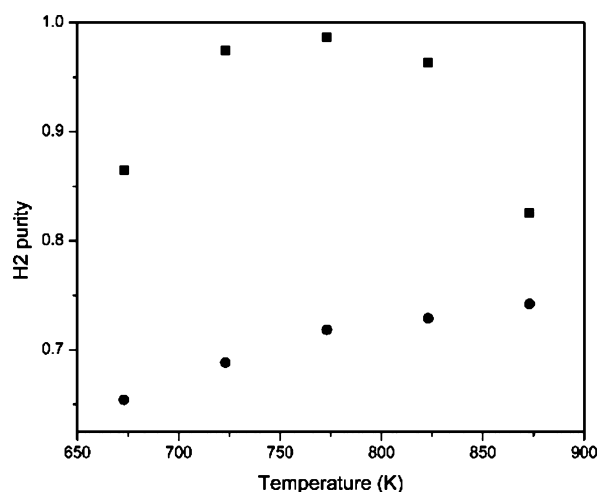
Figure 6. H_2 purity in the periods Pre-B and Post-B for different reaction temperatures: m_{cat} = 620 mg; m_{CaO} = 880 mg; R = 5.5; well-mixed configuration; (■) Pre-B; (●) Post-B.

Figure 7. CO_2 purity in each reaction cycle. m_{cat} = 620 mg; m_{CaO} = 880 mg; R = 5.5; reaction temperature = 823 K; regeneration temperature = 1123 K; well-mixed configuration. (■) This test; (dash line) ESR.

At the other extreme, at 673 K there is a considerable decrease in the H_2 purity and yield. This is attributed to the fact that at 673 K MSR is incomplete and equilibrium has not been reached.[6]

Unlike the period Pre-B, during the Post-B stage the variation is greater with the temperature since the behavior is determined by the endothermicity of the ESR. The difference in the purity of H_2 between the periods Pre-B and Post-B becomes significantly smaller, as the temperature increases. This is a consequence of the fact that the carbonation reaction is exothermic and becomes thermodynamically unfavorable with the increase in temperature; an increase in the reaction temperature decreases the sorption capacity of the solid, leading to a less efficient system.

Multiple cycles of carbonation−calcination were performed to analyze the stability of the system. For this test, the bed was loaded with the well-mixed configuration of catalyst (620 mg) and CaO (880 mg), and the reaction was carried out on average for 10 min, always at 823 K. The regeneration was implemented by increasing the temperature in a N_2 atmosphere, up to 1123 K with a ramp of 10 K/min, maintaining the final temperature for 5 min. This methodology was repeated until completing 20 cycles, while recording the composition of the product at 5 min from the beginning of each reaction cycle.

When operating in a cyclic way, a process of sintering of the sorbent takes place, which, as previously reported, generates a loss of sorption capacity. As the cycle number increases, the sorbent capacity decreases until cyclic steady state (CSS) is attained. In Figure 7 it is shown that from cycle 5 onward the CO_2 purity stays at an average value of 2.4%. In Table 3 the purities of H_2, CO, and CO_2 for cycles 1, 5, and 20 are reported.

The molar fraction of CO, defined on a wet basis, at the outlet of the WGS reactor is close to 2%.[12] In this test, the obtained CO concentration is lower than that value for at least 20 cycles in the period Pre-B (Figure 8), so the use of the WGS reactor in the purification train could be avoided if the SE-ESR process is used. Therefore, the purification section could be simplified due to higher H_2 purity and lower CO and CO_2 compositions, reducing investment costs due to a lower
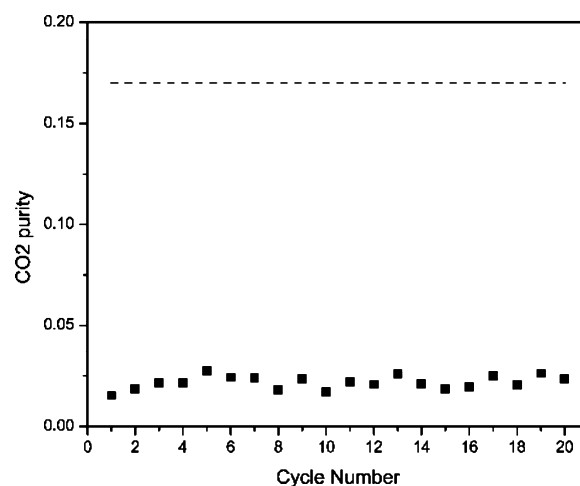
Table 3. H_2, CO_2, and CO Purities at Different Reaction Cycles[a]

	cycle 1	cycle 5	cycle 20
H_2	96.3%	95.0%	92.0%
CO_2	1.8%	2.4%	2.4%
CO	0.8%	1.9%	2.4%

[a]m_{cat} = 620 mg; m_{ads} = 880 mg; R = 5.5; reaction temperature = 823 K; regeneration temperature = 1123 K; bed configuration, homogeneous mixture.

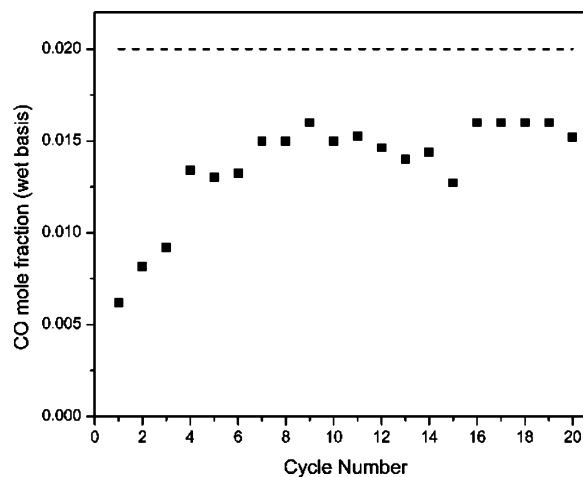**Figure 8.** CO mole fraction on a wet basis for each reaction cycle. m_{cat} = 620 mg; m_{CaO} = 880 mg; R = 5.5; reaction temperature = 823 K; regeneration temperature = 1123 K; well-mixed configuration. (■) This test; (dash line) WGS product stream.

number of operating units added to the possibility of operating the ES-ESR at a lower temperature than the ESR.[40]

4. CONCLUSION

SE-ESR was performed on a fixed-bed reactor with LDH NiMgAl as a catalyst precursor and CaO as a sorbent in order to investigate the effect of different catalyst-sorbent configurations, mass of CaO, and temperature.

It was found that the greater is the specific area, the greater is the CO_2 sorption capacity of the CaO sorbent. This is attributed to the presence of micropores that facilitate the diffusion of CO_2 into the CaO particles. After successive high temperature regenerations, the sintering process decreases the proportion of smaller pores (less than 100 Å) and therefore the capacity of sorption.

The highest H_2 purity is achieved with the well-mixed configuration and the purity of CO is also lower than that in the ESR. By increasing the sorbent/catalyst mass ratio, longer breakthrough period duration, higher H_2 purity, and lower CO_2 and CO contents were obtained in breakthrough period. For the tested relationships, there was no appreciable variation in the concentration of products in the prebreakthrough period.

It is emphasized that in the range of 723 K to 823 K the purity of H_2 in the prebreakthrough period reaches the highest value without significant variation, which is advantageous when thinking about the large-scale operation where isothermicity is difficult to maintain. This behavior is a result of the exothermicity of the adsorption that compensates the endothermicity of the ESR, so there is no evidence of a temperature dependence in the prebreakthrough period.

Finally, it is concluded that in the cyclic process, it is possible to obtain a product of stationary composition: high purity H_2 (92.0%) with a CO concentration of 1.65% on a wet basis, lower than that obtained in the purification train after the WGS reactor. It was verified that the SE-ESR process, using LDH NiMgAl as precursor of the catalyst and CaO as sorbent, simplifies the production of high purity H_2, eliminating the need of using the WGS reactor in the purification train.

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