

The effectiveness of dolomite and Ni-catalyst mixtures for pure H₂ production by methane steam reforming via CO₂ capture

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Abstract

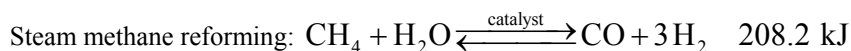
High hydrogen yields have been obtained continuously from steam reforming of methane coupled with simultaneous CO₂ capture[1], at lower temperature (630°C) and pressure (1 atm) than those typical of traditional processes (800-900°C, 15-30 atm), using calcined dolomite and a pulverized commercial Ni catalyst, in a single step. On the other hand, a pure CO₂ stream is obtained by subsequent regeneration of the sorbent, which could be stored. A bubbling fluidized bed contained in a quartz vessel was operated batchwise. First, the durability of a dolomite in multi-cycle CO₂ sorption/desorption runs has been investigated: a remarkable reduction of dolomite activity is observed after the first calcination, but substantially stable activity was conserved up to the fifth cycle. Then the performance of sorption enhanced catalytic steam reforming of methane to pure hydrogen has been evaluated. Two well distinct operation regimes have been found: before dolomite saturation, H₂ concentration in the dry product gas remained stable at 94-96%, and CO₂ was completely converted into calcium carbonate; after a short breakthrough period, concentration of H₂ at the exit of the reactor reduced its value that became approximately equal to the equilibrium value expected for methane reforming and water gas shift reactions.

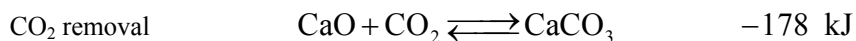
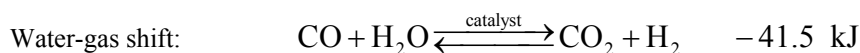
1. Introduction

Thermodynamic investigations

For the hydrogen production, conversion of natural gas via steam reforming with addition of a CO₂ sorbent is a promising process[2, 3]. By removing CO₂ as it is formed by the sorbent carbonation reaction, according to the Le Chatelier moderation principle, more methane is converted to hydrogen by its reforming and water gas shift reactions.

In the presence of a Ca-based sorbent as dolomite, the important reactions are:





The heat released by the exothermic carbonation reaction supplies most of the heat required by the endothermic reforming reaction.

Thermodynamic calculations using the “series reactor model” implemented by Chemcad© Process simulator provide the equilibrium concentrations as a function of temperature, with and without CO_2 sorbent. Fig. 1 shows that pure hydrogen production can be obtained at temperatures around 650°C by the reaction system shown above, and CO_2 is almost completely captured in the presence of CaO .

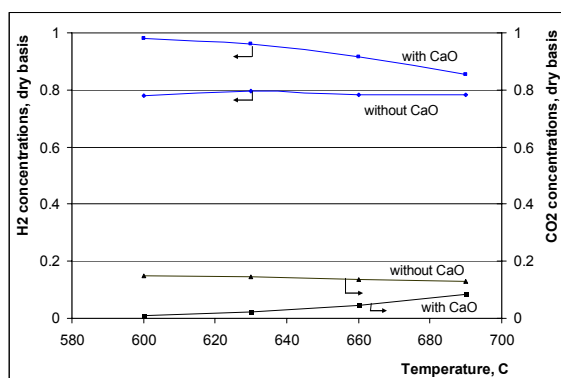


Fig. 1. Equilibrium hydrogen and CO_2 concentrations as a function of temperature

2. Experimental

Dolomite calcination/carbonation cyclic steps

Natural dolomite and a commercial Ni catalyst were crushed and sieved separately, to obtain fractions with average diameter of $200 \mu\text{m}$ and $300 \mu\text{m}$, respectively. The evaluation of the minimum fluidization velocity of dolomite and catalyst was performed experimentally by measuring the pressure drop (ΔP) at ambient temperature. A sample of about 100 g was fluidized in a cylinder with diameter 30 mm. Air was used as the fluidizing medium. For the dolomite sample, with density 1490 g/cm^3 , the measured minimum fluidization velocity is 3.19 cm/s, while for the catalyst sample, with density 1146 g/cm^3 , is 7.4 cm/s.

Calcination tests with a dolomite sample of about 200 g have been carried out in nitrogen atmosphere at 850°C in a proper designed laboratory- quartz reactor with ID 55 mm. At that temperature dolomite is fully calcined. In the carbonation tests, the bed of dolomite, previously calcined and kept at room temperature and under N_2 atmosphere, has been first heated up to 850°C , then exposed to a carbon dioxide (12-15%) in N_2 atmosphere, and finally cooled down slowly to 700°C and maintained at this temperature level till the end of reaction. Because of the high exothermicity of the re-carbonation

reaction, this procedure has been adopted to allow for a moderate re-carbonation rate, obtained by keeping the sorbent always close to equilibrium conditions. After test, the bed is left to cool naturally to ambient temperature, under N₂. The re-carbonation process does not affect the MgO fraction[4], which after the first calcination is not carbonated any more at the test temperature, because this is higher than its equilibrium calcination temperature (400°C). However this partial loss of CO₂ capturing capacity is balanced by a beneficial effect on the particle porosity that is kept higher during the CaO carbonation reaction, resulting in a lower deactivation level for cyclic operation conditions, than that observed with the utilization of limestone.

In the calcination tests, the attainment of the state of complete calcination is detected by CO₂ disappearing in the outlet gas, as well as by bed weighting before and after test. For the re-carbonation tests, the return to the initial composition of the feeding gas is utilised to stop the run.

Figure 2 shows the sorbent mass in the reactor, before and after each calcination/carbonation step, and the CO₂ mass absorbed and lost, all expressed in grams. The noticeable differences existing between the first calcination step and the subsequent ones have to be attributed to the behaviour of MgO recalled above.

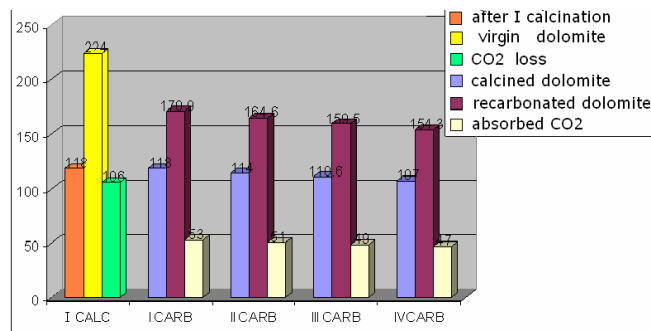


Fig.2. Dolomite behavior in cyclic calcination/carbonation steps.

One-step methane steam reforming to obtain hydrogen

After calcination, dolomite was mixed with a commercial Ni-based catalyst. The reduction of catalyst was performed in a H₂/N₂ atmosphere at 850°C, with 10.7% H₂ initial composition (molar fraction).

The experimental rig is shown in Fig. 3. During the H₂ production phase, CH₄ and N₂ were fed from high purity cylinders, and their flow rates were controlled using mass flow meters. Water was fed using a dosing pump, at a fixed steam to methane ratio equal to 4. The reaction tests have been performed at 630°C and 1 atm. The reactor is heated by a cylindrical electric furnace, equipped with a temperature recording and controlling system based on the data acquisition program PICOLOGGER. The composition of the gas leaving the reactor is determined using a gas analyzer ABB URAS 14. During the reforming period, the methane steam-reforming, the water-gas shift and the CO₂ absorption reactions take place simultaneously in one reactor.

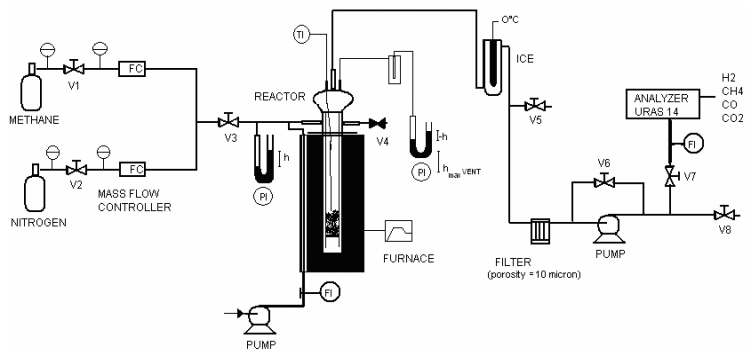


Fig. 3. Schematic view of the methane steam reforming and CO₂ capture system

3. Results

Results for the cyclic steam reforming of methane coupled with CO₂ capture are shown in figure 4, where the mole percentages of H₂, CO, CO₂, CH₄ in the product gas are plotted versus time.

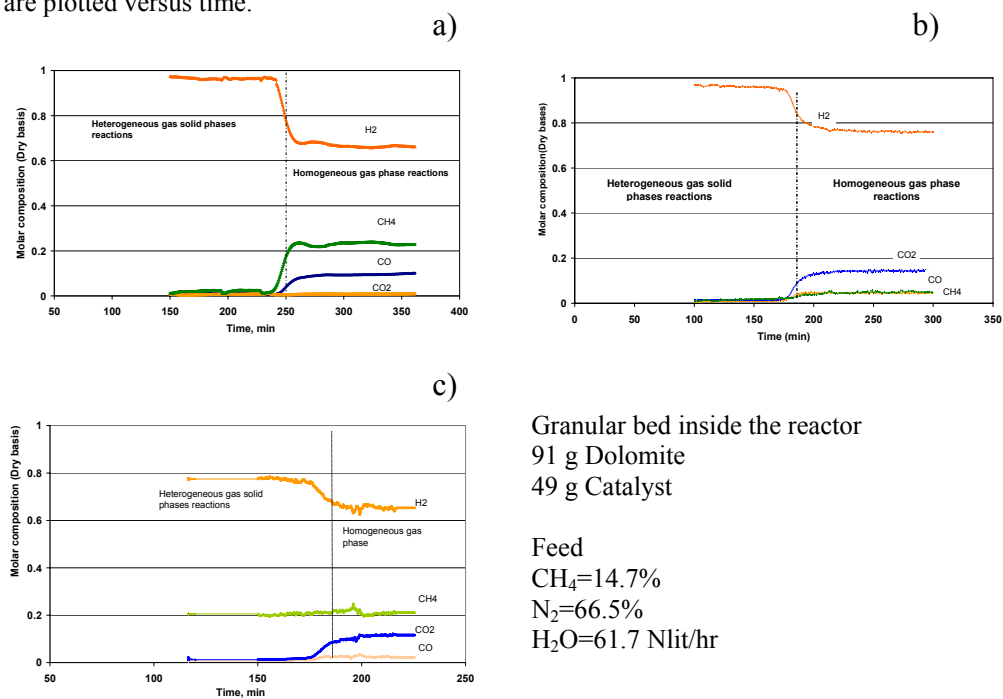


Fig. 4. Gas compositions (dry basis) as a function of time (min).

The vertical line on the figures corresponds to the time when the CO₂ sorption capacity of CaO initially charged in the reactor should be exhausted. Before breakthrough time, CO₂ concentration is brought to zero, and H₂ content in the product gas is very high. After breakthrough, the H₂ concentration decreases, whereas the CH₄, CO, CO₂ concentrations increase. Experimental results show that the mixture of dolomite and catalyst has been active and completely regenerated each time. Experimental molar concentrations measured after breakthrough are utilized to calculate the equilibrium temperature approach relative to methane steam reforming and water gas shift reactions: values very close to the effective reactor temperature have been found.

Fig. 4 and Table 1 show that the concentration of H₂ remained at 94-96% and CO₂ is zero in each cycle, which indicates good activity of both, catalyst and dolomite, in the cyclic tests. After the breakthrough condition is reached, the concentration of CO₂ in the product gas increases, as a result of the exhaustion of dolomite sorption capacity.

Tab.1. Experimental Results

Mol %, dry, N ₂ free basis	I cycle		II cycle		III cycle		Test without preliminary catalyst reduction with CO ₂ capture
	with CO ₂ capture	without CO ₂ capture	with CO ₂ capture	without CO ₂ capture	with CO ₂ capture	without CO ₂ capture	
H ₂	0.940	0.670	0.960	0.77	0.77	0.65	0.180
CO ₂	0.005	0.008	0.010	0.13	0.01	0.10	0.0002
CH ₄	0.010	0.230	0.010	0.04	0.20	0.22	0.820
CO	0.010	0.096	0.007	0.04	0.007	0.02	0.000

As shown in the last column of Table 1, a methane steam reforming test has been carried out without the preliminary reduction of catalyst; however in this case it was not possible to obtain a detectable H₂ yield at the same temperature level as in the previous tests.

3. Conclusion

From the experimental tests we can conclude that at “lower” values of temperature and pressure (630°C, 1 atm) than those typical at the traditional process conditions (800-900°C, 15-30 atm) high hydrogen yields and concentrations can be obtained by using dolomite as an effective CO₂ sorbent, mixed with a commercial Ni reforming catalyst, in

a fluidized bed natural gas-steam reformer. Dolomite needs to be calcinated cyclically, to recover its CO₂ sorption capacity. The catalyst needs to be reduced before each methane reforming step.

References

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