

Fluidized bed sorption-enhanced methanation by CaO

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Abstract

Methane appears to be a suitable energy vector which could both store solar energy and use fossil fuel derived CO₂ in the framework of CCU technologies. Moreover, methane has an already existing supply and storage infrastructure. The methanation reaction from hydrogen and carbon dioxide (or monoxide) is generally carried out in staged adiabatic fixed beds operated at high pressure in order to overcome thermodynamic limitations. The sorption-enhanced methanation concept is based on the employment of a sorbent which is able to capture *in situ* the H₂O produced during the reaction, in order to shift equilibrium towards the formation of methane. In this work CaO, derived from natural limestone, is tested as sorbent material for H₂O capture in a sorption-enhanced methanation configuration based on the concept of chemical looping in dual interconnected fluidized bed systems. The experimental campaign was focused on the study of the sorbent performance in terms of hydration and dehydration cycles at different operating conditions. The results showed that CaO has good capacity to capture and release steam in the temperature range of interest for methanation. Unfortunately, even at the lowest temperatures tested, the sorbent is affected by the presence of CO₂ that worsen its performance in terms of H₂O capture capacity.

Introduction

Methane is an important energy carrier for many sectors such as industry, household and transportation. The largest source of methane is represented by fossil resources (natural gas), but the growing debate on the utilization of fossil fuels in the framework of climate change has stimulated a growing interest towards catalytic and biological paths to synthetic methane production [1-3]. In particular, the catalytic methanation reaction ($4\text{H}_2 + \text{CO}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$ or $3\text{H}_2 + \text{CO} = \text{CH}_4 + \text{H}_2\text{O}$), discovered by Sabatier and Senders in 1902 [4], assumes an important role when combined with the concepts of chemical storage, solar fuels and utilization of CO₂. Methane could be considered as the final product for the storage of solar energy, initially converted into hydrogen by water splitting [5]. Unlike hydrogen, the main advantage of methane is the current existence of a well-developed distribution and storage infrastructure in many countries. Furthermore, methane benefits from a relatively large public acceptance. In addition, methanation could be considered as a process for the utilization of CO₂ coming from fossil fuels in the framework of Carbon Capture and Utilization (CCU) technologies [6]. The conventional methanation process typically requires a cascade of adiabatic fixed bed reactors with intermediate cooling steps and recycles [1,7] and high operational pressure to yield a product matching the specification for injection in the natural gas infrastructure. Borgschulte et al. [8] and Walspurger et al. [9] studied the possibility to improve the methanation process by the application of the concept of Sorption-Enhanced Methanation (SEM), where the steam generated by the reaction is continuously removed from the gas phase in the catalytic bed by adding a suitable sorbent material, e.g. a zeolite, so as to drive the equilibrium towards CH₄ formation.

In this study a novel configuration for SEM based on the technology of dual interconnected fluidized beds is investigated. The concept is based on a chemical looping reactor arrangement where the catalytic methanation occurs simultaneously with H₂O capture in one reactor (methanator/hydrator), while sorbent regeneration takes place in another reactor (dehydrator).

Experimental

The sorbent tested in this work was CaO obtained by calcination at 850°C of a German limestone named EnBW. The experimental apparatus used for the tests consists of two identical lab-scale bubbling beds of silica sand, acting as thermal ballast, operated batch-wise and connected by a rapid solids transfer line. This device is used to study looping processes, and a complete description is reported elsewhere [10]. The two reactors were employed as hydrator and dehydrator respectively. The experimental campaign was aimed at evaluating the suitability of CaO to capture and release water at different relevant conditions.

The main operating conditions were: hydration with 10% steam (balance air) and dehydration in nitrogen or in air. A preliminary sensitivity analysis on temperature was first carried out fixing the hydration temperature at 250°C and varying the dehydration temperature at 350, 400 and 450°C in nitrogen (tests: H25A-D35N, H25A-D40N, H25A-D45N), and subsequently fixing the dehydration temperature at 400°C and varying the hydration one at 200, 250 and 300°C (tests: H20A-D40N, H25A-D40N, H30A-D40N). The progress of hydration and dehydration reactions was followed during the tests by measuring the concentration of steam at the outlet by means of a humidity sensor. The H₂O capture capacity of the material was evaluated after each cycle for 4 complete cycles, while the fluidization velocity was fixed at 0.5m/s. The time of each hydration or dehydration step was fixed at 15 min. The exhaust materials were analyzed by a TG device to evaluate the amount of captured CO₂.

Another set of tests was carried out fixing the temperature of both hydration and dehydration at 200 and 400°C respectively, and using air (instead of nitrogen) as fluidizing gas during the dehydration stages, in order to investigate possible detrimental effect of CO₂ (contained in the air) on the sorbent performance: these tests were named H20A-D40A.

Finally, the effect of high levels of CO₂ was also studied during the hydration stage introducing CO₂, 1 and 10% by volume, together with steam. The temperatures during the two stages were 200°C for hydration and 400°C for dehydration. These conditions produced the tests named H20A1C-D40N and H20A10C-D40N. In Table 1 the investigated conditions are summarized.

Table 1. Main operating conditions of the hydration/dehydration tests.

	Temperature	Fluidizing gas		
		H ₂ O	CO ₂	Balance
H25A-D35N	250/350 (°C)*	10/0 (%vol)	400/0 (ppm)	Air/Nitrogen
H25A-D40N	250/400 (°C)			
H25A-D45N	250/450 (°C)			
H20A-D40N	200/400 (°C)			
H30A-D40N	300/400 (°C)		400/400 (ppm)	Air/Air
H20A-D40A	200/400 (°C)			
H20A1C-D40N	200/400 (°C)			
H20A10C-D40N	200/400 (°C)			
			1/0 (%vol)	Air/Nitrogen
			10/0 (%vol)	

*the first value (250) refers to the hydration stage, the second one (350) to the dehydration stage. This notation is valid for all couples of values in the table.

Results and Discussion

Figure 1 shows the measured H₂O capture capacity of CaO, expressed as gram of H₂O captured per gram of initial sorbent, as a function of the cycle number at different dehydration (fig.1A) and hydration (fig.1B) temperatures. The capture capacity seems to increase with the dehydration temperature after the first cycle, with a maximum around the 2nd-3rd cycle for H25A-D40N and H25A-D45N, while the value remains nearly constant for H25A-D35N (fig.1A). This behavior may be explained by the fact that different dehydration temperatures could alter the microstructure of the CaO with a consequent variation in sorbent capacity. On the contrary, the capture capacity decreases with the hydration temperature (fig.1B). This trend is probably due to the increasing role of carbonation by CO₂ (present in air) at higher hydration temperatures. Apparently, the effect of the hydration temperature vanishes after 4 cycles.

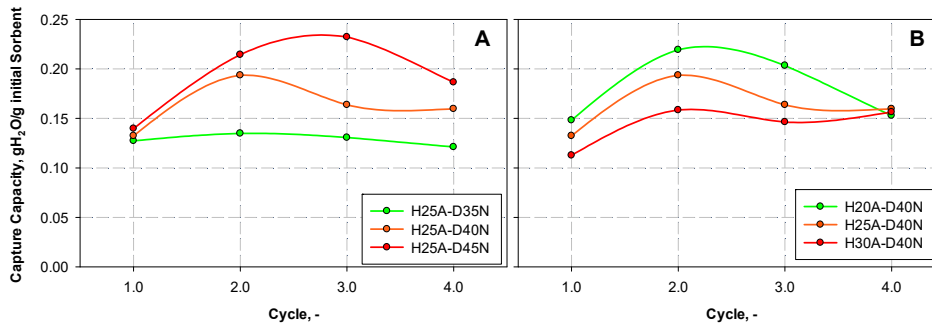


Figure 1. H₂O capture capacity of the sorbent along cycles: effect of the dehydration temperature (A) and of the hydration temperature (B).

When nitrogen was substituted by air during the dehydration stage, the presence of additional CO₂ determined a detrimental effect which increased with the number of cycles. This is showed in Figure 2A where the H₂O capture capacity measured in tests H20A-D40N (in black) and H20A-D40A (in blue) are compared. It is clear, just after the first cycle, that there is a difference between the values of the two tests (as expected) and this is mainly due to the additional carbonation of CaO during the dehydration stages. Despite the CO₂, the curve still shows an increase of hydration capacity after the first cycle, demonstrating that the phenomenon related to the microstructural change after the first dehydration is still active.

The effect of a high concentration of CO₂ during the hydration stage is shown in Figure 2B. The red curve refers to the test with CO₂ at 1% (H20A1C-D40N), and a negative effect with respect to the black curve (H20A-D40N), where CO₂ was not added, is clearly visible. The increase of the hydration capacity (after the first dehydration) is still present, but to a reduced extent. The decrease of the hydration capacity was about 67% for the first cycle, about 75% for the fourth.

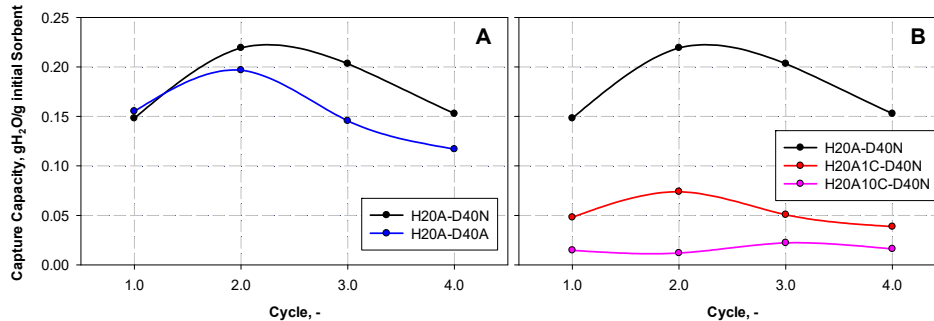


Figure 2. H₂O capture capacity of the sorbent along cycles: effect of the presence of low (A) and high (B) levels of CO₂ during the hydration stages.

When the percentage of CO₂ was increased at 10% (pink curve - H20A10C-D40N), the hydration capacity of CaO decreased further, and the maximum observed in all the other conditions disappeared. The curve is practically flat with a value of the hydration capture which is around 0.016g H₂O/g of sorbent. This probably means that the carbonation process is so prominent to limit the microstructural effects after the first dehydration.

However, the sole carbonation does not completely explain the observed detrimental effect on the hydration capture; in fact, from the analysis (by thermogravimetry) on the exhaust sorbents H20A-D40N and H20A10C-D40N the carbonation degrees were measured to be about 11.7 and 12.6% by mass respectively, which are not dramatically different. This seems to indicate the presence of an additional effect caused by CO₂. For this reason, a specific test was conceived where the first two cycles were carried out under H20A10C-D40N conditions (with the presence of 10% CO₂ during the hydration stage), while the third and the fourth cycle were operated under H20A-D40N conditions (in absence of additional CO₂ during the hydration stage). Figure 3 shows the

measured H₂O capture capacity during this ‘hybrid’ test. It is possible to note that for the first two cycles the capture capacity showed values similar to those obtained for the test H20A10C-D40N (see Fig.2B), but when the additional CO₂ to the hydrator was turned off (from the third cycle) an increase of the H₂O capacity occurred. This behavior cannot be explained only with the carbonation reaction, since this reaction is irreversible at the operating temperatures employed in the tests, and a permanent decrease of the H₂O capacity should have been observed. Possibly, an additional inhibition effect by CO₂ to the hydration reaction takes place under the conditions investigated, but further investigation is clearly necessary to explain this effect.

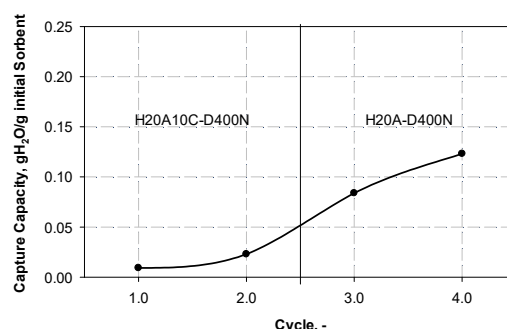


Figure 3. H₂O capture capacity of the sorbent along cycles: effect of the variable presence of CO₂ during the hydration stage.

Conclusions

CaO showed good H₂O capture capacity in the temperature range of interest for catalytic methanation. Cyclic hydration/dehydration tests demonstrated the potential of *in situ* steam uptake in a dual fluidized bed chemical looping reactor. Important results were obtained as to the competition between CO₂ and H₂O for the sorbent, which may negatively impact selective H₂O capture in the presence of CO₂. However, the mechanism of the inhibition by CO₂ of the H₂O capture is not completely clear and deserves deeper studies. Moreover, further tests are necessary to measure the attrition tendency of the CaO particles under these conditions.

These results encourage the use of CaO for SEM with CO, while suggest the need to search for alternative more selective sorbents for methanation with CO₂.

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