FLUIDIZATION XVI

Testing different sorbents for sorption-enhanced methanation in a dual fluidized bed system

Antonio COPPOLA, Fiorella MASSA, Piero SALATINO, Fabrizio SCALA

Istituto di Ricerche sulla Combustione
Consiglio Nazionale delle Ricerche

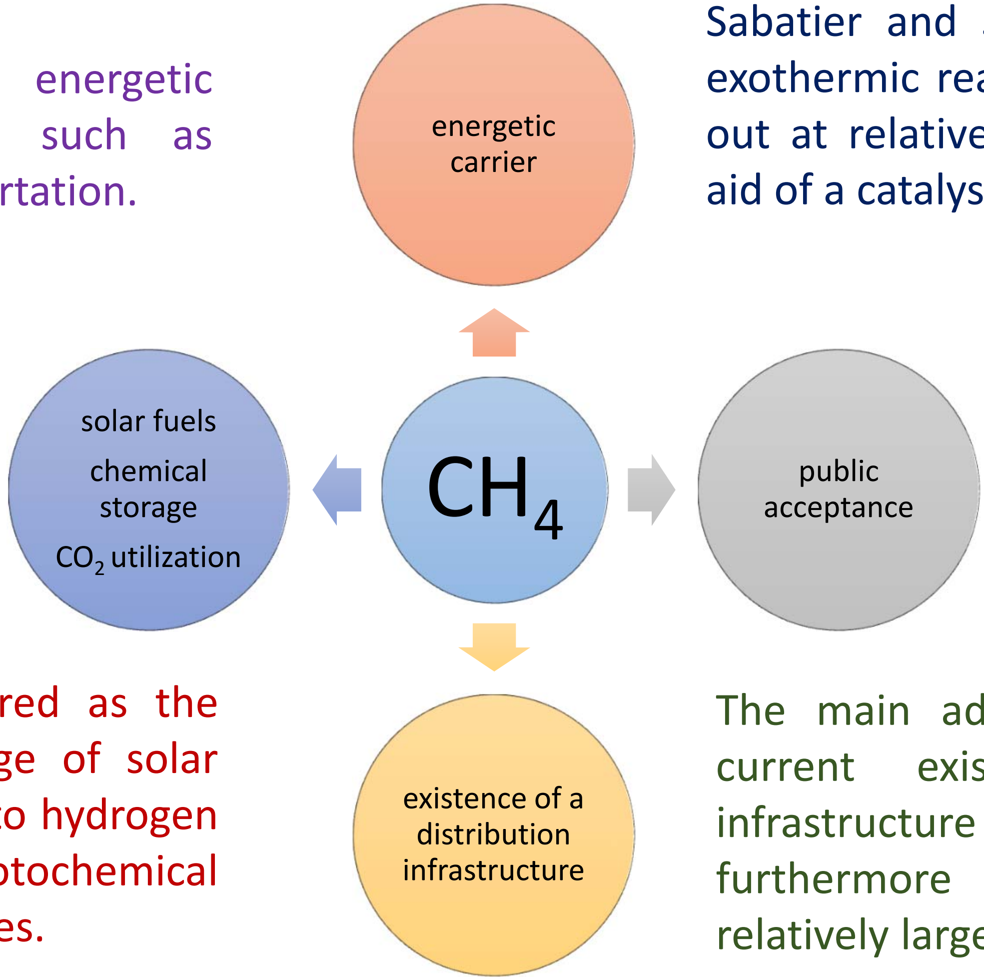
DICMaPI
Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale
Università degli Studi di Napoli Federico II

INTRODUCTION

Methane is an important energetic carrier for many sectors such as industry, energy and transportation.

Methanation is one interesting option for CO_2 utilization in the framework of Carbon Capture and Utilization (CCU).

Methane could be considered as the final product for the storage of solar energy, initially converted into hydrogen by water splitting with photochemical and thermochemical processes.



The methanation reaction, discovered by Sabatier and Senders in 1902, is a highly exothermic reaction, which must be carried out at relatively low temperature with the aid of a catalyst.

CO Methanation

$$CO + 3H_2 = CH_4 + H_2O\ (g)$$

-206 kJ/mol

CO_2 Methanation

$$CO_2 + 4H_2 = CH_4 + 2H_2O\ (g)$$

-164 kJ/mol

The main advantage of methane is the current existence of a distribution infrastructure in many countries; furthermore methane benefits from a relatively large public acceptance.

INTRODUCTION

Reactor types for CO/CO_2 methanation

- Fixed bed reactors(c)
- Fluidized bed reactors(d)
- Structured reactors(r)
- Three phase reactors(r)

(c) Commercial Scale
(d) Demonstration Scale
(r) Research

The conventional methanation process typically requires a cascade of adiabatic fixed bed reactors with intermediate cooling steps and recycles and high operational pressure to yield a product matching the specification for injection in the natural gas infrastructure.

Sorption Enhanced Methanation (SEM)

Borgschulte et al. (2013) and Walspurger et al. (2014) proposed 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.

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$$

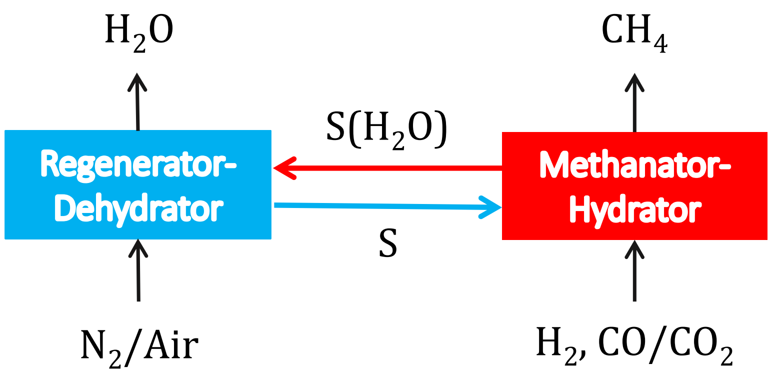
$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$$

Sorbent

Chemical Looping Sorption Enhanced Methanation (CLSEM)

- A novel SEM configuration based on dual interconnected fluidized beds is proposed.
- The concept relies on a chemical looping arrangement where catalytic methanation occurs simultaneously with sorbent hydration in one reactor (methanator/hydrator), while sorbent regeneration takes place in another reactor (regenerator/dehydrator).
- The materials tested as possible sorbents were CaO derived from natural limestone and a zeolite (3A).

$$S(H_2O) = S + H_2O$$



$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

$$CO + 3H_2 = CH_4 + H_2O$$

$$S + H_2O = S(H_2O)$$

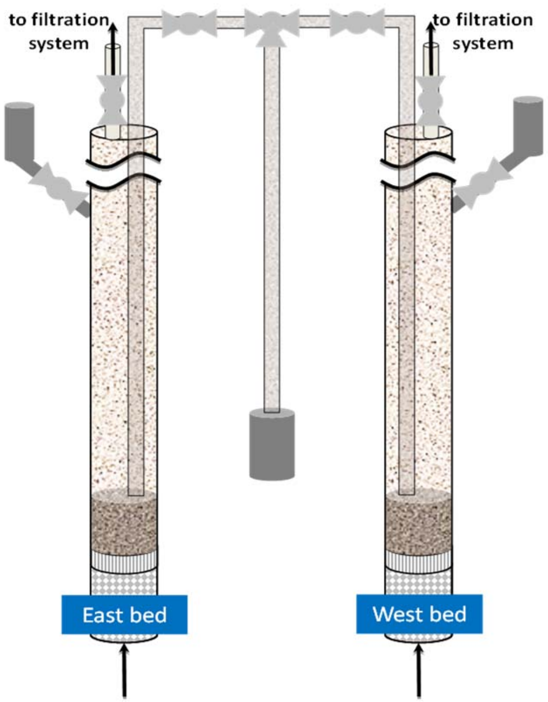
Istituto di Ricerche sulla Combustione
Consiglio Nazionale delle Ricerche
DICMaPI
Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale
Università degli Studi di Napoli Federico II

Experimental

Sorbents: CaO - 3A Zeolite

Calcined @850°C from natural limestone

Commercial



Hydration/Dehydration Tests

Evaluation of the **H_2O capture capacity** of the material was evaluated after each cycle for **10 complete cycles**

T (°C)	**200-450°C**
Fluidizing Gas	Air (+H_2O)
U (m/s)	0.5
Time (min)	10
Sorbent	CaO, Zeolite
Bed Material	Silica Sand, 900-1000 µm

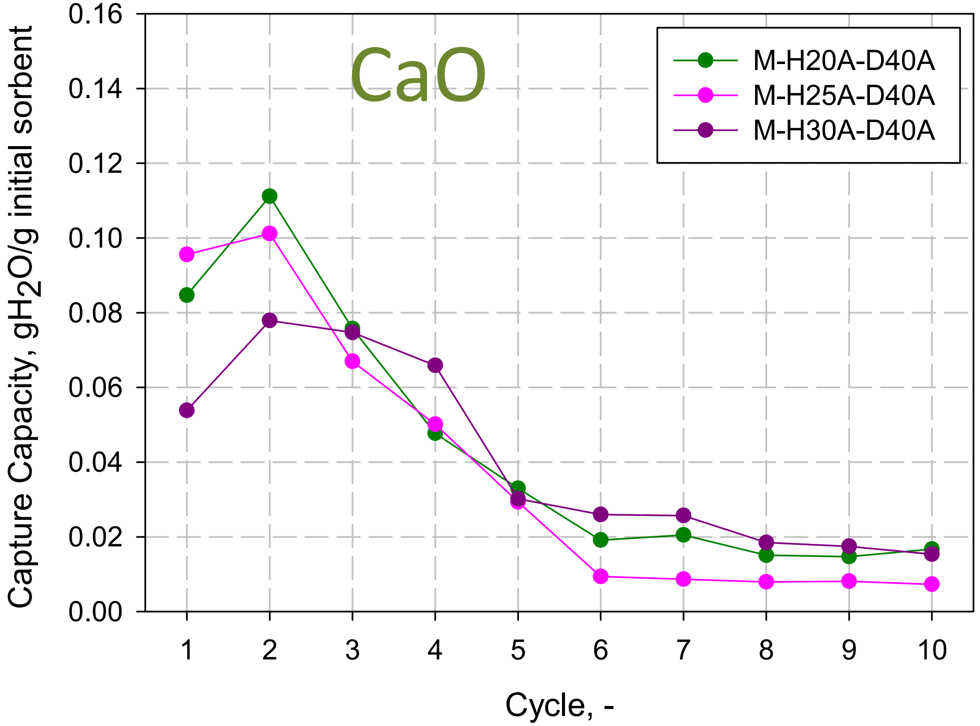
Experimental

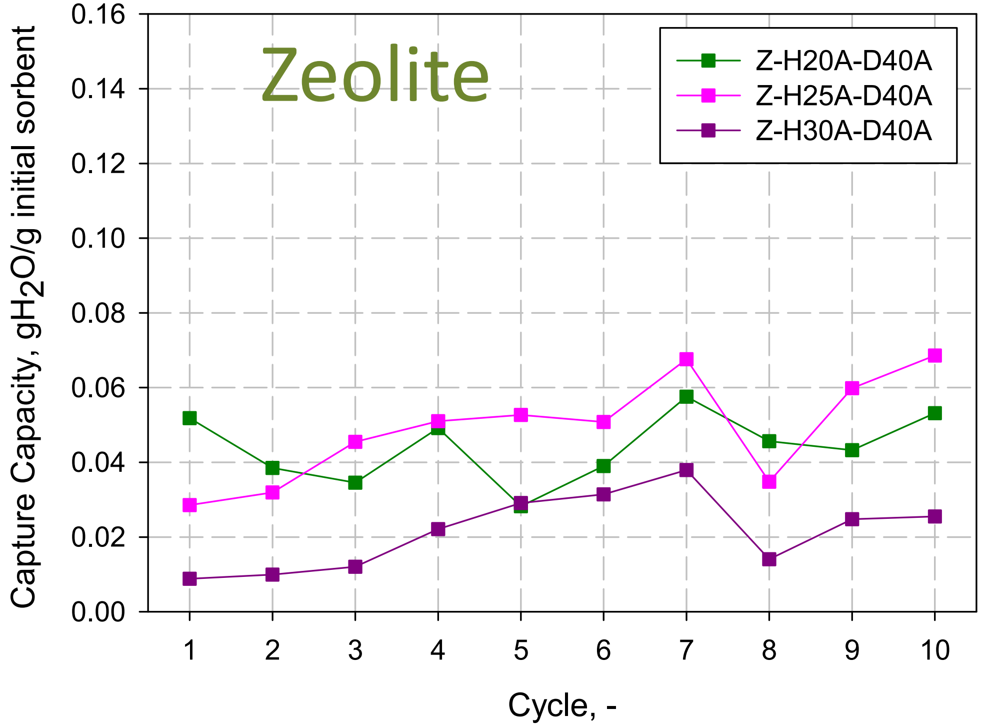
X=M (CaO), Z (Zeolite)

	Temperature	Fluidizing gas		
		H_2O	CO_2	Balance
X*-H20A-D35A	200/350 (°C)	10/0 (%vol)	400/400 (ppm)	Air/Air
X-H25A-D35A	250/350 (°C)			
X-H25A-D40A	250/400 (°C)			
X-H25A-D45A	250/450 (°C)			
X-H30A-D35A	300/350 (°C)			
X-H30A-D40A	300/400 (°C)			
X-H30A-D45A	300/450 (°C)			

Results: T-Sensitivity

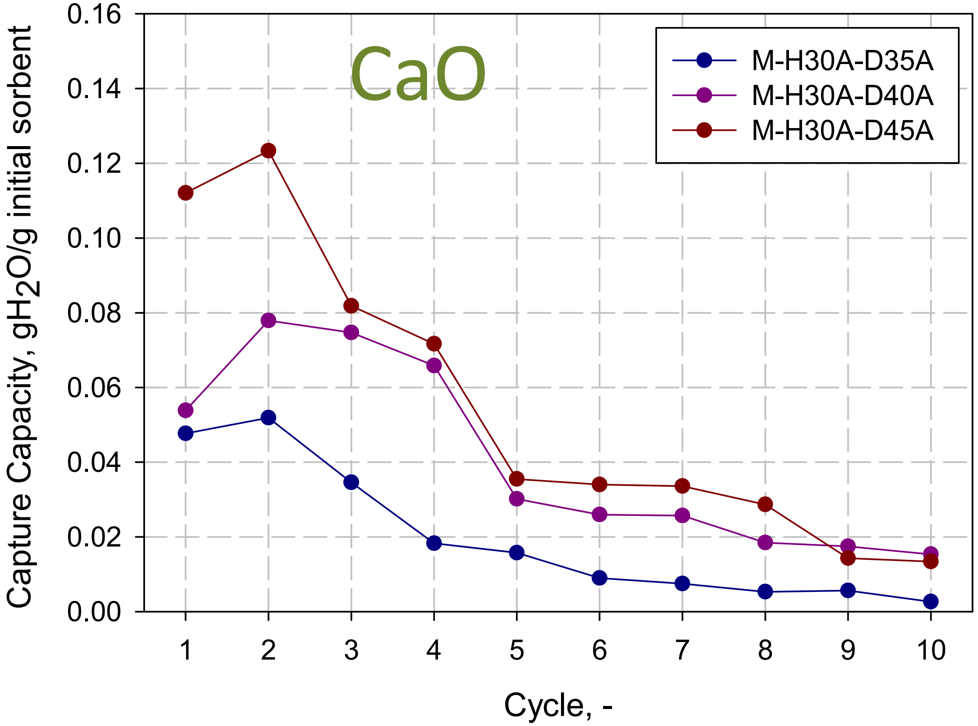
Hydration: 200, 250, 300°C
Dehydration: 400°C

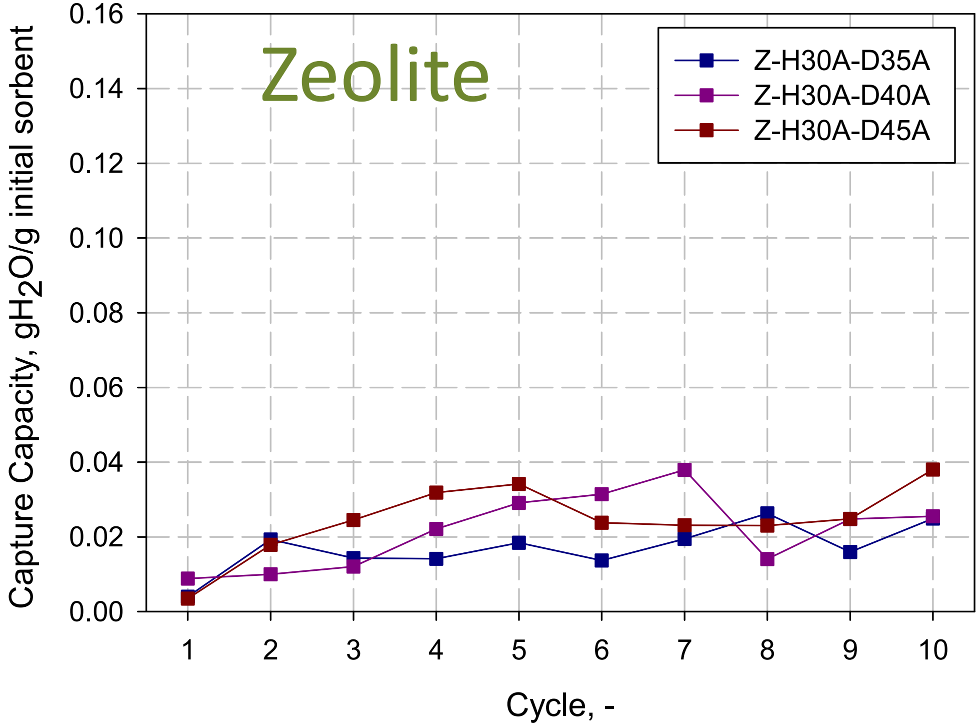




Results: T-Sensitivity

Hydration: 300°C
Dehydration: 350, 400, 450°C





Conclusions

- Results for CaO showed, for all conditions investigated, that the H_2O capture capacity had a maximum around 2nd-3rd cycle, and successively it decreased with number of cycles, reaching an asymptotic value, due to progressive sorbent carbonation.
- An increase of the dehydration temperature induced an increase of the capture capacity. This behavior could be determined by a change of the sorbent microstructure. A positive effect was also registered when increasing the hydration temperature.
- As opposed to CaO, for the Zeolite 3A no decay effect with the number of cycles was observed. However, the hydration temperature had an opposite effect: the higher the hydration temperature, the lower the sorbent capacity. The dehydration temperature seems to have no remarkable effect on the zeolite performance.

FLUIDIZATION XVI

Testing different sorbents for sorption-enhanced methanation in a dual fluidized bed system

A. Coppola, F. Massa, P. Salatino, F. Scala

Istituto di Ricerche sulla Combustione
Consiglio Nazionale delle Ricerche

DICMaPI
Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale
Università degli Studi di Napoli Federico II

Thank you for your attention