

# Integrated CO<sub>2</sub> Capture and Catalytic Methanation over Dual Function Materials in a Lab-Scale Interconnected Fluidized Bed System

Fiorella Massa<sup>1</sup>, Elisabetta Maria Cepollaro<sup>1</sup>, Stefano Cimino<sup>1</sup>, Antonio Coppola<sup>1</sup>,  
Fabrizio Scala<sup>1,2\*</sup>

*1 STEMS, CNR, P.le Tecchio 80, Napoli, Italy;*

*2 DICMaPI, Università di Napoli Federico II, P.le Tecchio 80, Napoli, Italy;*

*\*Corresponding author: [fabrizio.scala@unina.it](mailto:fabrizio.scala@unina.it)*

## **Highlights**

- Integrated CO<sub>2</sub> capture and methanation is tested in dual interconnected fluidized beds.
- Dual function materials show good stability and reproducibility during cycles.
- By physically separating the two steps it is possible to effectively optimize the process.

## **1. Introduction**

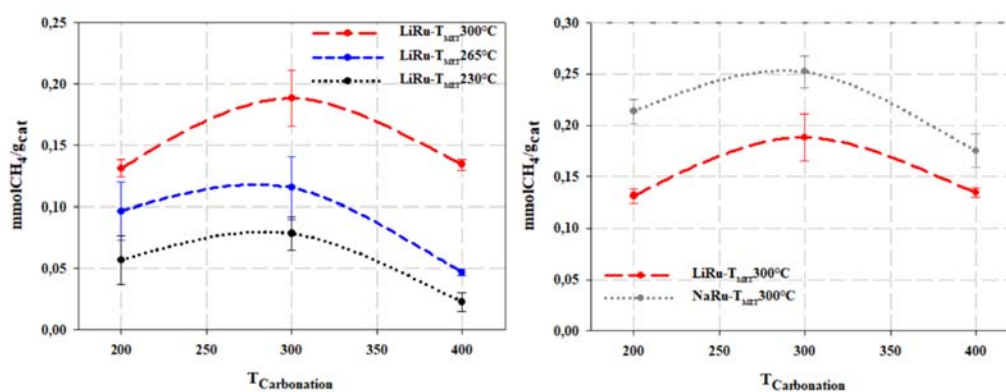
Integrated CO<sub>2</sub> capture and reduction (ICCR) solutions have been recently proposed to reduce the cost and increase the efficiency of the current carbon capture and utilization processes, characterized by energy-intensive regeneration steps [1]. These techniques are based on the use of dual function materials (DFM), which combine both sorbent and catalyst functionalities to capture and convert CO<sub>2</sub> from a point source into synthetic fuels (e.g. methane) via the reaction with green H<sub>2</sub>, thus resulting in a chemical looping process. DFMs include alkaline or alkaline earth components for CO<sub>2</sub> capture, and Ni or Ru as the active phase for CO<sub>2</sub> hydrogenation to CH<sub>4</sub>. Based on the study by Cimino et al [2], we prepared two Ru-based DFMs containing a low loading of noble metal (1% wt.) co-dispersed together with 5% wt. Li or Na on commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> spheres characterized by high mechanical resistance. Herein we propose a chemical looping process based on the use of two interconnected fluidized beds. Such a reactor configuration would allow the steady operation of the process, where the DFM particles can be continuously transported between a CO<sub>2</sub> capture reactor and a methanation reactor, thus overcoming one of the main drawbacks of fixed beds, due to their inherent discontinuous operation.

## **2. Methods**

The two DFMs were prepared following the procedure reported in [2]. The experimental campaign was carried out in a batch lab-scale apparatus consisting of two identical stainless steel bubbling fluidized beds conceived with the aim of studying looping processes by enabling the fast pneumatic transport of granular material between the two reactive environments [3]. CO<sub>2</sub> capture and its subsequent methanation were investigated at the temperatures of 200, 300 and 400 °C and 230, 265 and 300 °C, respectively. After loading the DFM (about 20 g), 5% CO<sub>2</sub> in N<sub>2</sub> stream was fed to the reactor for 8 min (carbonation) followed by purging 2 min in pure N<sub>2</sub> before the DFM was transferred to the other reactor. The hydrogenation in the second reactor, started with a flow of 4% H<sub>2</sub> in N<sub>2</sub> fed for a total duration of 8 min, followed by 2 min of N<sub>2</sub> purging. Five complete cycles of carbonation and hydrogenation were carried out for each test condition.

## **3. Results and discussion**

The performance of Li-Ru DFM was quite stable and reproducible over the cycles, which were characterized by a rapid increase of the CH<sub>4</sub> production, followed by a slower decrease due to the progressive depletion of the captured CO<sub>2</sub> available on the DFM as reactant for methanation. The overall outlet amount of methane was calculated by integration of the temporal concentration profiles and averaged over the cycles for all the tests performed (Fig.1 - left). When considering carbonation, as expected for an exothermic chemisorption process, the CO<sub>2</sub> uptake decreased with increasing the temperature from 300 °C to 400 °C. However, at the lowest carbonation temperature of 200 °C, a lower CH<sub>4</sub> production occurred, since CO<sub>2</sub> was thermally released from the DFM in the purge phase before H<sub>2</sub> was fed to the methanation reactor which was always at a higher temperature than the carbonator.



**Figure 1.** Average methane production under all the test conditions with Li-Ru DFM (left), and comparison of the tests with Li-Ru and Na-Ru DFMs at the methanation temperature of 300 °C and different carbonation temperatures (right).

As expected, for each carbonation temperature, methane production increased along with the increase of the methanation temperature from 230 to 300 °C due to kinetic limitations. Notably, the CO outlet concentration was negligible under all tested conditions and the methane yield approached 100%. Turning to the Na-promoted DFM, the trend of the CH<sub>4</sub> production still showed good reproducibility over the cycles but differed from the Li-promoted case: the peak value was significantly lower and delayed. Due to the slower kinetics of the catalytic reaction, longer times were required to convert the pre-captured CO<sub>2</sub> into methane. Despite the slower kinetics, the total amount of CH<sub>4</sub> produced was higher under the investigated conditions (Fig.1 - right). However, the higher methane production was associated with lower yields, i.e. 73 and 91% at the carbonation temperatures of 300 and 400 °C, respectively. Furthermore, the Na-Ru DFM material presented a lower selectivity compared the Li-promoted one, being the amount of CO produced not negligible.

#### 4. Conclusions

A chemical looping integrated CO<sub>2</sub> capture and methanation process, based on the use of two interconnected fluidized beds, was investigated in a lab-scale apparatus. The DFMs performance appeared to be quite reproducible over the cycles, but it was subject to kinetic limitations, especially in the case of Na-Ru/Al<sub>2</sub>O<sub>3</sub>. Interestingly, the methane yield approached 100% under the highest tested temperatures for the Li-based DFM. Despite some limitations due to the experimental purge phases of the lab-scale system, the study provides the proof-of-concept of the process which enables the possibility of decoupling the two steps with a large potential intensification. In particular, physically separating the adsorption and hydrogenation phases would allow to split the exothermicity of the whole process and to optimize each single step in terms of operating parameters.

#### Acknowledgements

The authors acknowledge funding from the project PNRR - Partenariati estesi - “NEST - Network 4 Energy Sustainable Transition” - PE0000021. Fiorella Massa and Elisabetta Cepollaro acknowledge funding from the European Union - NextGenerationEU under the National Recovery and Resilience Plan (NRRP), Mission 04 Component 2 Investment 3.1, Project Code: IR0000027 - CUP:B33C22000710006 - iENTRANCE@ENL: Infrastructure for Energy TRAnSition aNd Circular Economy @ EuroNanoLab

#### References

- [1] S. Omodolor, H.O. Otor, J.A. Andonegui, B.J. Allen, A.C. Alba-Rubio, Dual function materials for CO<sub>2</sub> capture and conversion: a review, *Ind. Eng. Chem. Res.* 59 (40) (2020).
- [2] S. Cimino, F. Boccia, L. Lisi, Effect of alkali promoters (Li, Na, K) on the performance of Ru/Al<sub>2</sub>O<sub>3</sub> catalysts for CO<sub>2</sub> capture and hydrogenation to methane, *J. CO<sub>2</sub> Util.* 37 (2020) 195–203.
- [3] A. Coppola, F. Scala, L. Gargiulo, P. Salatino, A twin-bed test reactor for characterization of calcium looping sorbents, *Powder Technology* 316 (2017) 585–591.

#### Keywords

CO<sub>2</sub> Capture; Methanation; Dual Function Materials; Fluidized Beds; Chemical Looping.