

Parametric Study of Methanation Performance on Ru/Na₂O/Al₂O₃ Dual-Function Materials

Andrea Strazzolini, Andrea Braga, Maila Danielis, Sara Colussi*

Dipartimento Politecnico e INSTM, Università degli Studi di Udine, 33100 Udine, Italy

sara.colussi@uniud.it

The development of Dual-Function Materials (DFMs) for the combined CO₂ capture and valorization is gaining increasing attention due to its process intensification approach and promising advantages in terms of energy requirements. Significant efforts are devoted to optimizing materials and process configuration, but on both sides many issues still remain open. In this work the behavior of dry milled Ru/Na₂O Dual-Function Materials on an alumina-based support with different methanation kinetics is evaluated for the coupled CO₂ capture and hydrogenation to methane. In particular, the duration of the methanation step is changed to investigate its effect on the overall efficiency of the material, measured in terms of both CH₄ yield and H₂ conversion. The results show that, by opportunely tuning this parameter, it is possible to increase the average specific methane production rate by a factor of 1.9 or 2.6, the improvement being all the more significant the faster the CO₂ methanation kinetics, increasing also the noble metal utilization efficiency.

1. Introduction

Re-using waste CO₂ as a carbon feedstock for the production of e-fuels is considered an attractive solution to mitigate the greenhouse gas emissions while also shifting the society reliance on fossil to renewable fuels (Aresta and Dibenedetto 2024). However, CO₂ conversion requires a significant amount of energy due to the kinetic and thermodynamic limitations correlated with its stability. The separation, compression, and transportation steps are also energy-intensive, which coupled with the production of H₂, a necessary co-reagent, might reduce the net balance of CO₂ reduction. To maximize the impact of CO₂ utilization, renewable H₂ should be used which adds further complexity and costs to the system (Gao et al. 2020). In this regard, the integrated carbon capture and utilization (CCU) approach represents an interesting solution. The CO₂ is separated by adsorption on the same solid material where the valorization occurs in a subsequent step by simply switching the feed gas, thus decreasing the energy requirements of the separation, compression, and transportation steps. Key elements of this approach are the so-called Dual-Function Materials (DFMs), which contain both the adsorbent and the catalytic active phase, usually represented by an alkali phase and a metal, respectively, co-dispersed on a support oxide (Zhang et al. 2024). Conventional compositions are based on Ni and Ru catalytic sites, and Na, K or Ca-based oxides for the CO₂ capture function dispersed on high-surface oxides such as γ -Al₂O₃. Most studies are dedicated to the improvement of the DFMs formulation, trying to enhance capture capacity and CH₄ selectivity, and in this respect mechanochemically prepared materials have shown promising results both on the adsorbent phase (Stefanelli et al. 2023) and on the full DFMs (Danielis et al. 2024). The parametric analysis of the process operating conditions (partial pressure, temperature, flow rates, cycle time) can also be used to increase the overall methane yield and hydrogen consumption efficiency, as the availability of renewable hydrogen is a key factor for the overall sustainability of the process (Huang et al. 2025). These aspects are crucial to define the best operating conditions for the cyclic operation of DFMs. A quite recent work highlights how the cycle time can be used to optimize the efficiency of DFMs (Bermejo-López et al. 2022). The authors introduce the average CH₄ formation rate ($\mu\text{mol g}^{-1} \text{s}^{-1}$) as a suitable parameter to evaluate the methanation efficiency of the material. However, this parameter does not consider the noble metal efficiency, Ru being the most expensive component, and its value depends on the criteria adopted to set the methanation step duration hindering a straightforward comparison between different DFMs. Despite the relevance of

parametric analysis, there are still only a few papers that address these issues and among them, to the best of our knowledge, only a couple compare the effect of different parameters on different DFMs (Chen et al. 2024; Buelens et al. 2025), limiting general conclusions. Moreover, there is a lack of investigation where both material properties and process parameters are taken into account. Chen et al. performed a sensitivity study for ICCU choosing various DFMs from the literature, but due to the heterogeneous nature of the starting data their results can give only a preliminary background, without a direct correlation between material-process parameters. The paper by Buelens et al. is focused mostly on material properties affecting selectivity, CO₂ capture capacity and stability, not considering changes in operating conditions apart from the addition of steam. In this work, the methanation behavior of two mechanochemically prepared Ru/Na₂O-based DFMs with different kinetics is compared, to investigate the effect of cycle time keeping into account also the kinetics of the material. The study of two analogous samples is aimed at the evaluation of the combined effect of an external, adjustable parameter with that of an intrinsic one, allowing a rational and more general comparison among different DFMs.

2. Materials and methods

Details of the Dual-Function Materials synthesis and their testing procedures are reported in the following.

2.1 DFMs preparation

DFMs were prepared relying on a previously developed dry milling procedure (Danielis et al. 2024), adapted to obtain materials with different kinetics (Braga et al. 2024). Na and Ru precursors were co-milled on a γ -Al₂O₃ support in a single-step dry ball milling process by loading appropriate amounts of Ru acetylacetonate (Strem Chemicals) and Na₂CO₃ (Carlo Erba) with γ -Al₂O₃ powders to obtain respectively 1 wt% of Ru and 10 wt% of Na₂O equivalent. To obtain different methanation kinetics, two γ -Al₂O₃ supports were employed: one unpromoted (SASOL) and the other with 10 wt% Ce_{0.75}Zr_{0.25}O_x (W.R. Grace & co.). The sample prepared on non-promoted pure Al₂O₃ (herein: R-N) was milled at 15 Hz for 60 min in a 50 mL ZrO₂ jar using a Retsch MM500 mill, while the promoted (R-N-CZ) DFM was milled for 27 min at 27 Hz in a 15 mL ZrO₂ jar using a Fritsch Pulverisette 23 mini-mill. The ball-to-powder weight ratio (BPR) was fixed equal to 9 in both cases. No further calcination treatments were performed on the DFMs before testing.

2.2 DFMs characterization

Surface area and pore size measurements were carried out using a Nova 800 Analyzer (Anton Paar) measuring physisorption isotherms at -196 °C in N₂. The specific surface areas and the pore size distributions were estimated using the Brunauer-Emmett-Teller (BET) and the Barrett-Joyner-Halenda (BJH) methods, respectively. Prior to the analysis, all samples were outgassed in vacuum at 150 °C for 1.5 h.

2.3 Integrated capture and methanation activity evaluation

The DFMs were tested for the cyclic capture and methanation of CO₂ (ICCU-MET) in a fixed-bed quartz reactor (12 mm ID), loading 250 mg of DFM powder on a quartz wool bed and placing a thermocouple above the catalytic bed. Before testing, a pretreatment in 10% H₂/N₂ (10 °C min⁻¹ to 400 °C, 1 h holding time) was performed. Then, the temperature was reduced at 350 °C and the sample was exposed alternatively to 50 mL min⁻¹ of 5% CO₂/N₂ (capture step) and 50 mL min⁻¹ of 10% H₂/N₂ (methanation step) with a 100 mL min⁻¹ N₂ purge step in between. The capture step time was kept fixed at 5 min, while the methanation step time was varied between 3, 5, and 10 min. In total, five cycles were performed for each test. The evolution of H₂, CO₂, CO and CH₄ was followed online with an ABB AO2020 analyzer recording data points every 5 s. The molar flows were integrated to obtain the moles of CO, CO₂ and CH₄:

$$n_{i,OUT} = \frac{1}{m_{DFM}} \int_{t_0}^{t_1} \dot{F}_i(t) dt \quad (1)$$

Where $i = (\text{CO}, \text{CO}_2, \text{CH}_4)$, m_{DFM} is the DFM mass loaded in the reactor, and \dot{F}_i is the molar flow. The cumulative CH₄ production (P_{CH_4} , $\mu\text{mol g}^{-1}$) versus time along the methanation step was calculated by integrating the CH₄ molar flow starting from the beginning of the step, according to equation (2). The same equation was used to evaluate the stepwise specific CH₄ yield by evaluating the integral over the entire step duration.

$$P_{CH_4}(t) = \frac{1}{m_{DFM}} \int_0^t \dot{F}_{CH_4}(t) dt \quad (2)$$

The CO₂ specific uptake rate (r_{CO_2} , $\mu\text{mol min}^{-1} \text{g}^{-1}$) was estimated from the measured CO₂ concentration at the reactor outlet by subtracting a blank measurement.

$$r_{CO_2} = \frac{1}{m_{DFM}} (\dot{F}_{CO_2, BLANK}(t) - \dot{F}_{CO_2}(t)) \quad (3)$$

The total CO₂ uptake (U_{CO_2} , $\mu\text{mol g}^{-1}$) during the capture step was calculated by integrating equation (3) over the entire capture step duration shown in equation (4).

$$U_{CO_2} = \int_{\text{Capture step}} (r_{CO_2}) dt \quad (4)$$

The H₂ conversion (X_{H_2} , %) was calculated by equation (5), where $n_{H_2, IN}$ and $n_{H_2, OUT}$ denote the moles of H₂ fed and the moles of H₂ measured at the reactor outlet, respectively, during the methanation step.

$$X_{H_2} = \frac{n_{H_2, IN} - n_{H_2, OUT}}{n_{H_2, IN}} \cdot 100 \quad (5)$$

3. Results and Discussion

The use of a dry mechanochemical method for the preparation of DFMs was previously reported to enable improved CO₂ capture and CO production in ICCU-RWGS applications (Danielis et al. 2024) compared to conventionally prepared DFMs by wet impregnation (Merkouri, Ramirez Reina, and Duyar 2022). However, synthesis parameters such as metal and alkali precursors, number of milling steps, and calcination steps, led to Dual-Function Materials with different properties (Danielis et al. 2024). Here, the same approach was exploited to obtain DFMs with different methanation kinetics. The addition of a promoter (Ce_{0.75}Zr_{0.25}O₂) was explored, as Ce-doping is known to improve the methanation kinetics on Ru/Al₂O₃ catalysts (Tada et al. 2014). The summary of the textural properties of the DFMs, such as the specific surface area, cumulative pore volume, and average pore size, are reported in Table 1. In particular, it appears clearly that the addition of Ce_{0.75}Zr_{0.25}O₂ reduces the surface properties of alumina, leading to smaller pores and a slight loss of pore volume and surface area. However, the specific surface area values are still quite similar (80 vs 100 m² g⁻¹ for R-N-CZ and R-N, respectively), allowing a fair comparison in terms of catalytic performance.

Table 1: Summary of main textural properties of prepared DFMs.

Sample short name	Full formulation	Surface area (m ² g ⁻¹)	BJH pore volume (cm ³ g ⁻¹)	Average pore size (nm)
R-N	1 wt% Ru / 10 wt% Na ₂ O / Al ₂ O ₃	100	0.50	15
R-N-CZ	1 wt% Ru / 10 wt% Na ₂ O / 10 wt% Ce _{0.75} Zr _{0.25} O ₂ / Al ₂ O ₃	80	0.28	9

Figure 1 compares the CO₂ specific uptake rate of the unpromoted and the CZ-promoted sample. Both DFMs show a sharp uptake profile, with most of the CO₂ capacity filled within the first 1.5 minutes. The CZ modification improved the capture capacity of the DFM, which may be ascribed to the additional sorption capacity provided by the CZ itself (Yoshikawa et al. 2014) rather than a surface area effect, as shown in Table 1. The total CO₂ uptake for the two samples was estimated to be 284.5 and 323.4 $\mu\text{mol g}^{-1}$ for the non-promoted and the CZ-containing sample, respectively.

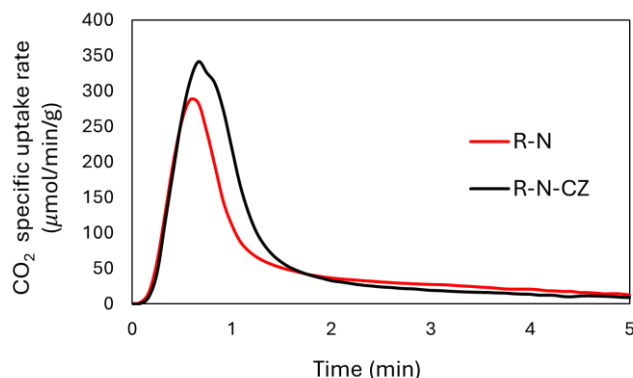


Figure 1: Comparison between the CO₂ specific uptake rate of R-N and R-N-CZ during a typical capture step.

Figure 2a compares the cumulative CH₄ production of the unpromoted (R-N) and the Ce_{0.75}Zr_{0.25}O₂-promoted sample (R-N-CZ) during a 10 minutes methanation step. Both samples show a fast CH₄ production at the beginning of the step, with almost superimposable curves. Between 1.5 and 8 minutes, instead, the two samples exhibit different patterns. R-N sample shows a limited increase in cumulative CH₄ production, whereas R-N-CZ continues producing methane, albeit at a slower rate. Thus, the modification with CZ led to a net increase in the total CO₂ adsorption capacity of the material without affecting the fast CO₂ release capability of the DFM in the first part of the methanation step. Instead, it provided additional adsorption sites with a slower desorption-methanation kinetics, which start to react approximately after 1.5 minutes, when the majority of the “fast” adsorption sites are consumed. The selectivity towards CH₄ is higher than 97% for both samples (Figure 2b). For the R-N sample, the main byproduct is unconverted CO₂ while for R-N-CZ some CO formation is observed.

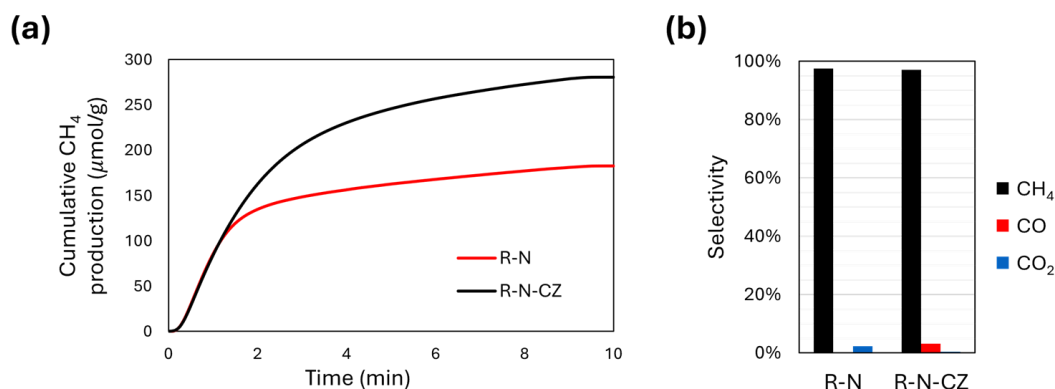


Figure 2: (a) Cumulative CH₄ production and (b) product distribution of the unpromoted (R-N) and CZ-promoted (R-N-CZ) sample during a typical methanation step. Both capture and methanation were performed at 350 °C.

The effect of varying the cycle time for the hydrogenation step on the R-N sample is shown in Figure 3a. A cyclic steady state was attained by performing 5 capture-methanation cycles for each condition (data in the plot refer to the 5th cycle). CH₄ production shows a sharp onset soon after H₂ is fed to the reactor. The CH₄ productivity reaches a maximum within 1 minute, then experiences a quick drop to below 20% of the maximum value. By comparing the quantitative amount of CO₂ captured and CH₄ produced, it clearly appears that the CO₂ adsorbed by the DFMs during the capture step is largely made available for conversion at the start of the methanation step, utilizing a significant portion of the material's total adsorption capacity. This reactivity pattern implies that reducing the cycle time significantly enhances the average CH₄ productivity of the step. By reducing the step time from 10 to 5 and 3 minutes, the average productivity is incremented by a factor of 1.9 and 2.6, respectively. Since the sorbent is largely regenerated at the beginning of the step, shortening the step time has a limited effect on both the methanation kinetics and the effective CO₂ sorption capacity. As shown in figure 3b, increasing the cycle time from 5 to 10 minutes clearly penalizes the H₂ conversion without producing a proportional increase of the stepwise CH₄ yield, because H₂ is fed without additional reactivity. This may provide advantages in ICCU systems that are designed to operate with fast cycling and in cases where a high single-pass H₂ conversion is required, depending on the system design and the availability of green H₂. Indeed, the cost of H₂ is known to significantly affect the economics of integrated carbon capture and utilization systems (Qiao et al. 2023).

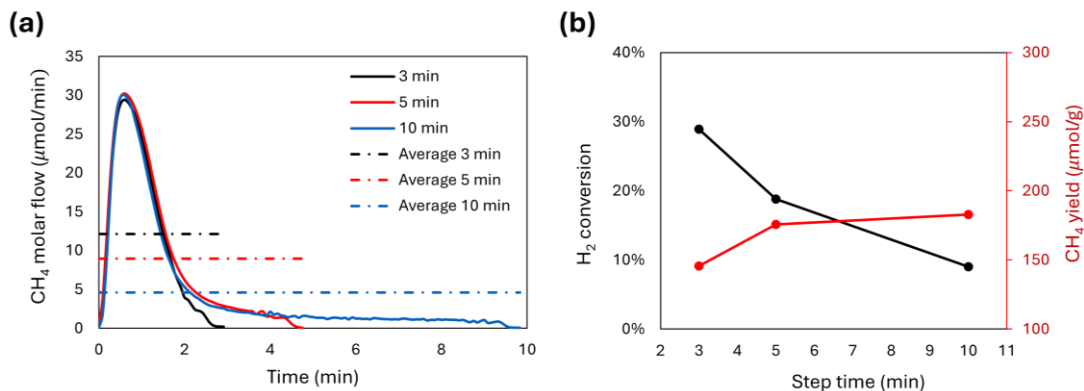


Figure 3: (a) Methane transient evolution at different methanation step duration for the R-N sample. The average values are reported as dashed lines. (b) H₂ conversion and specific CH₄ yield as a function of the methanation step time. Both capture and methanation were performed at 350 °C.

Figure 4a reports the CH₄ evolution of the Ce_{0.75}Zr_{0.25}O₂-promoted sample (R-N-CZ) at different step times. Similarly to the previous case, CH₄ evolves as soon as H₂ is fed to the reactor, and the productivity reaches its maximum within 1 minute. Then, a gradual decrease in the production rate is observed, with a slightly higher residual CH₄ production rate after 8 minutes of exposure to H₂ with respect to the previous case (1.63 vs. 1.06 $\mu\text{mol min}^{-1}$ of the R-N sample). Consequently, the stepwise average productivity is less affected by the step time adopted with respect of R-N because the CH₄ evolution is more spread along the step length. In this case, reducing the step time from 10 to 5 and 3 minutes increased the average productivity by a factor of 1.7 and 1.9, respectively, showing a limited increase in productivity at 3 minutes compared to the R-N sample (2.6 times increase). This also implies that more time on stream is required to regenerate the sorbent. As shown figure 4b, increasing the step duration leads to a sensible increase in the total CH₄ yield both between 3 and 5 minutes and between 5 and 10 minutes. In this case, finding a balance between the CH₄ yield and the H₂ conversion is less straightforward in respect to the previous case, and is consequently more dependent on the system design.

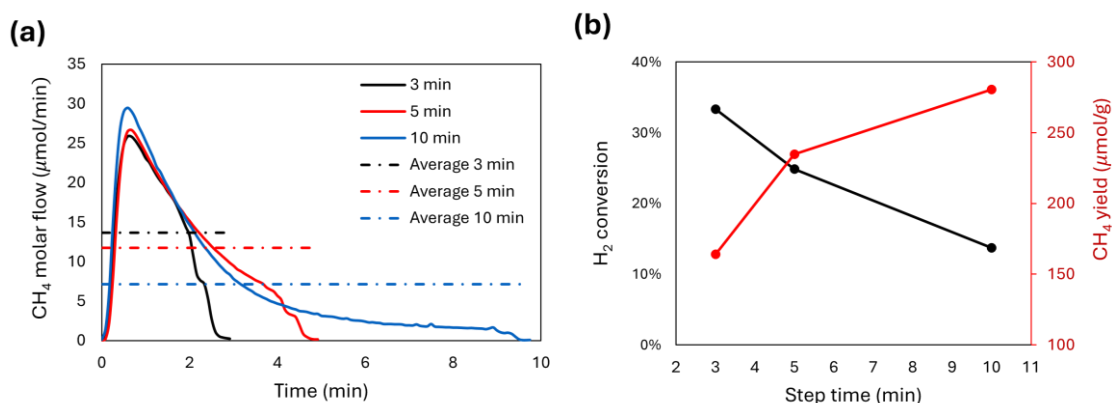


Figure 4: (a) Methane transient evolution at different methanation step duration for the R-N-CZ sample. The average values are reported as dashed lines. (b) H₂ conversion and specific CH₄ yield as a function of the methanation step time. Both capture and methanation were performed at 350 °C.

Table 2 summarizes the DFMs performance indicators previously discussed as a function of the methanation step duration. As an additional indicator, the average specific productivity is reported also on a Ru mass basis, since the material cost is presumably largely determined by the active metal loading. The values obtained on this mechanochemically prepared DFMs are comparable or superior to similar formulations prepared via conventional wet synthesis approach and tested under similar experimental conditions (Bermejo-López et al. 2022). From the results reported above, the steeper the CH₄ release profile, the higher the improvement in the average specific CH₄ production rate obtained by decreasing the cycle time, and the smaller is the penalty on the stepwise CH₄ yield. This finding requires some other parameter to correlate the cycle time duration with the catalytic kinetics, as it is clear that the overall efficiency depends on both properties. The optimal design of an ICCU system utilizing DFMs for the methanation reaction should carefully consider the intrinsic properties of the sorbent, including the CO₂ release dynamics, to meet the desired performance requirements.

Table 2: average total CH₄ production and specific CH₄ production rate for the two materials

Sample	Step time (min)	Total CH ₄ production ($\mu\text{mol g}^{-1}$)	$\Gamma_{\text{CH}_4, \text{avg}}$ ($\mu\text{mol g}^{-1} \text{min}^{-1}$)	$\Gamma_{\text{CH}_4}(\text{Ru})$ ($\text{mmol g}_{\text{Ru}}^{-1} \text{min}^{-1}$)
R-N	3	142.4	47.7	4.77
Ru/Na ₂ O/Al ₂ O ₃	5	174.6	34.9	3.49
	10	181.8	18.2	1.82
R-N-CZ	3	165.2	55.1	5.51
Ru/Na ₂ O/CZ/Al ₂ O ₃	5	234.9	47.0	4.70
	10	284.4	28.4	2.84

4. Conclusions

In this work the effect of the methanation step duration is investigated for two DFMs with comparable CO₂ adsorption dynamics but different methanation kinetics. From the comparison of the two samples, it appears that the shortening of the methanation step can be a valid strategy to maximize the average specific CH₄ production rate when the material has a fast methanation kinetics, with a positive impact also on the efficiency

of H₂ utilization that is a relevant aspect of ICCU-MET systems relying on renewable hydrogen. In particular, by reducing the step time from 10 to 3 minutes, an increase of 62% in CH₄ productivity per mole of ruthenium is observed. In the case of slower kinetics, instead, the methanation step duration is less relevant (48% productivity improvement per mole of Ru) and finding optimal operating conditions for both methane yield and hydrogen conversion is not straightforward. Overall, the results presented here clearly show that a combined analysis of system operating parameters and DFMs intrinsic properties, both catalytic and sorption, is required to operate the ICCU-MET process efficiently in light of an effective process intensification approach.

Acknowledgments

This study was carried out within the Interconnected Nord-Est Innovation Ecosystem (iNEST) and received funding from the European Union Next-Generation EU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) – MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.5 – D.D. 1058 23/06/2022, ECS00000043, CUP: G23C22001130006). M.D. is grateful for funding under the REACT EU Italian PON 2014–2020 Program – Action IV.4 – Innovation (DM 1062, 10/08/2021, CUP G51B21006040007). SC acknowledges funding by the European Commission under the framework of C-NET project, HORIZON-MSCA-2023-SE-01, Project reference: 101182598.

References

- Aresta, M., Dibenedetto, A., 2024, Merging the Green-H₂ Production with Carbon Recycling for Stepping towards the Carbon Cyclic Economy, *Journal of CO₂ Utilization*, 80, 102688.
- Bermejo-López, A., Pereda-Ayo, B., González-Marcos, J.A., González-Velasco, J.R., 2022, Simulation-Based Optimization of Cycle Timing for CO₂ Capture and Hydrogenation with Dual Function Catalyst, *Catalysis Today*, 394–396, 314–324.
- Braga, A., Danielis, M., Colussi, S., Trovarelli, A., 2024. Dataset for paper "Rational Screening of Milling Parameters for Ru-Na/Al₂O₃ Dual Function Materials for the Integrated CO₂ Capture and Methanation" [Data set]. Zenodo. <https://doi.org/10.5281/zenodo.14415918>.
- Buelens, L.C., Van der Voorde, L., Singh, V.J., Van Cauwelaert, M.W.F., Poelman, H., Van Geem, K.M., Galvita, V.V., 2025, *Chemical Engineering Journal*, 505, 159596.
- Chen, Y., Shen, L., Chen, L., 2024, Sensitivity study of integrated carbon capture and methanation process using dual function materials, *Separation and Purification Technology*, 344, 127170.
- Danielis, M., Merkouri, L.P., Braga, A., Trovarelli, A., Duyar, M.S., Colussi, S., 2024, Feasibility of Green Mechanochemical Synthesis for Dual Function Materials Preparation, *Journal of CO₂ Utilization*, 86, 102895.
- Gao, W., Liang, S., Wang, R., Jiang, Q., Zhang, Y., Zheng, Q., Xie, B., Toe, C.Y., Zhu, X., Wang, J., Huang, L., Gao, Y., Wang, Z., Jo, C., Wang, Q., Wang, L., Liu, Y., Louis, B., Scott, J., Roger, A.C., Amal, R., He, H., Park, S.E., 2020, *Industrial Carbon Dioxide Capture and Utilization: State of the Art and Future Challenges*, *Chemical Society Reviews*, 49, 8584-8686.
- Huang, Y., Liu, W., Yong, J.Y., Zhang, X., Wu, C., Jiang, L., 2025, Environmental Tradeoff on Integrated Carbon Capture and In-Situ Methanation Technology, *Renewable and Sustainable Energy Reviews*, 208, 115029.
- Merkouri, L.P., Ramirez Reina, T., Duyar, M.S., 2022, Feasibility of Switchable Dual Function Materials as a Flexible Technology for CO₂ Capture and Utilisation and Evidence of Passive Direct Air Capture, *Nanoscale*, 35, 12620–12637.
- Qiao, Y., Liu, W., Guo, R., Sun, S., Zhang, S., Bailey, J.J., Fang, M., Wu, C., 2023, Techno-economic analysis of integrated carbon capture and utilisation compared with carbon capture and utilisation with syngas production, *Fuel*, 332, 125972.
- Stefanelli, E., Vitolo, S., Malquori, S., Puccini, M., 2023, Li₄SiO₄-based Adsorbents for CO₂ Capture at High Temperature: Performance Enhancement by Ball Milling Process, *Chemical Engineering Transactions*, 100, 193-198.
- Tada, S., Ochieng, O.J., Kikuchi, R., Haneda, T., Kameyama, H., 2014, Promotion of CO₂ Methanation Activity and CH₄ Selectivity at Low Temperatures over Ru/CeO₂/Al₂O₃ Catalysts, *International Journal of Hydrogen Energy*, 19, 10090–10100.
- Yoshikawa, K., Sato, H., Kaneeda, M., Kondo, J.N., 2014, Synthesis and analysis of CO₂ adsorbents based on cerium oxide, *Journal of CO₂ Utilization*, 8, 34-38.
- Zhang, Y., Zhao, S., Li, L., Feng, J., Li, K., Huang, Z., Lin, H., 2024, Integrated CO₂ Capture and Utilization: A Review of the Synergistic Effects of Dual Function Materials, *Catalysis Science and Technology*, 4, 790–819.