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

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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 (ICCU) 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 (μmol g-1 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.

* 1. Materials and methods

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

* + 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% Ce0.75Zr0.25Ox (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.

* + 1. 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.

* + 1. 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:

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|  | (1) |

Where (CO, CO2, CH4), is the DFM mass loaded in the reactor, and is the molar flow. The cumulative CH4 production (PCH4, 𝜇mol 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.

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|  | (2) |

The CO2 specific uptake rate (rCO2,𝜇mol min-1 g-1) was estimated from the measured CO2 concentration at the reactor outlet by subtracting a blank measurement.

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|  | (3) |

The total CO2 uptake (UCO2, 𝜇mol g-1) during the capture step was calculated by integrating equation (3) over the entire capture step duration shown in equation (4).

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| --- | --- |
|  | (4) |

The H2 conversion (XH2, %) was calculated by equation (5), where nH2,IN and nH2,OUT denote the moles of H2 fed and the moles of H2 measured at the reactor outlet, respectively, during the methanation step.

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|  | (5) |

* 1. 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 (Ce0.75Zr0.25O2) 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 Ce0.75Zr0.25O2 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.

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| --- | --- | --- | --- | --- |
| Sample short name | Full formulation | Surface area  (m2 g-1) | BJH pore volume (cm3 g-1) | Average pore size (nm) |
| R-N | 1 wt% Ru / 10 wt% Na2O / Al2O3 | 100 | 0.50 | 15 |
| R-N-CZ | 1 wt% Ru / 10 wt% Na2O /  10 wt% Ce0.75Zr0.25O2 /Al2O3 | 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 𝜇mol g-1 for the non-promoted and the CZ-containing sample, respectively.

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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 Ce0.75Zr0.25O2-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.

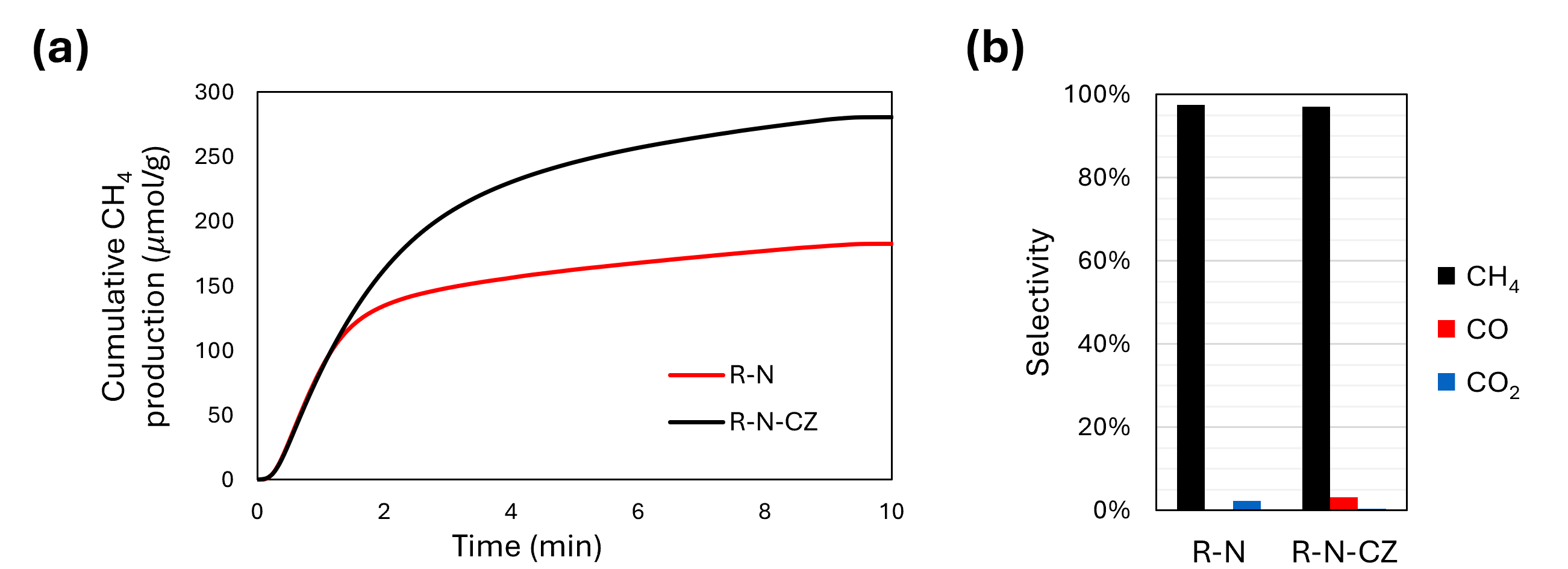


Figure 2: (a) Cumulative CH4production and (b) product distribution of the unpromoted (R-N) and CZ-promoted (R-N-CZ) sample during a typical methanation step. Both capture and methanation were performed at 350 °C.

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).

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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 Ce0.75Zr0.25O2-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 𝜇mol 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.

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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

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| --- | --- | --- | --- | --- |
| Sample | Step time (min) | Total CH4 production  (μmol g-1) | rCH4, avg  (μmol g-1 min-1) | rCH4(Ru)  (mmol gRu-1 min-1) |
| R-N Ru/Na2O/Al2O3 | 3 | 142.4 | 47.7 | 4.77 |
| 5 | 174.6 | 34.9 | 3.49 |
| 10 | 181.8 | 18.2 | 1.82 |
| R-N-CZ Ru/Na2O/CZ/Al2O3 | 3 | 165.2 | 55.1 | 5.51 |
| 5 | 234.9 | 47.0 | 4.70 |
| 10 | 284.4 | 28.4 | 2.84 |

**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.

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